

For Reference

NOT TO BE TAKEN FROM THIS ROOM

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex LIBRIS
UNIVERSITATIS
ALBERTAENSIS





Digitized by the Internet Archive
in 2019 with funding from
University of Alberta Libraries

<https://archive.org/details/Reid1964>

Thesis
1965
#152

THE UNIVERSITY OF ALBERTA

SOME FACTORS AFFECTING NITROGEN MOVEMENT, TRANSFORMATIONS,
AND UPTAKE IN ALBERTA SOILS

by

ARTHUR SELBOURNE JELF REID, B.S.A., M.S.A. (Toronto)

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF SOIL SCIENCE

EDMONTON, ALBERTA

NOVEMBER, 1964

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Some Factors Affecting Nitrogen Movement, Transformations, and Uptake in Alberta Soils" submitted by Arthur Selbourne Jelf Reid, B.S.A., M.S.A. (Toronto), in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Greenhouse and laboratory studies were conducted on Maleb and Cooking Lake soils with the objective of comparing the utilization of added N on these soils. An attempt was also made to study some of the factors affecting N movement, transformations, and uptake in these soils.

It appeared from these studies that the Maleb A horizon promoted the growth of barley in the presence of added N to a greater extent than did the Cooking Lake analogue, and provided a larger pool of available N from which the crop could draw. Applied N proved to be the dominant nutrient variable, and had a marked effect not only on the dry matter yield of barley but also on the uptake of N, K, and Ca.

Lime had a depressive effect on N uptake on the Maleb A horizon and to a lesser degree on the Cooking Lake soil. On the C horizon of both soils there was evidence that lime interfered with the uptake of K. The effect of added lime appeared to be similar to that of indigenous free lime in inhibiting N uptake on the different soils.

Applied K had no noticeable effect on the yields of dry matter, N, and Ca but did promote K uptake on the Maleb and Cooking Lake A horizons.

Tracer studies involving the use of $\text{N}^{15}\text{H}_4\text{NO}_3$ were conducted in an attempt to characterize the N equilibrium in the Maleb and Cooking Lake A horizons and also to investigate immobilization-mineralization phenomena in these soils. Rittenberg's apparatus for converting $\text{N}^{15}\text{H}_4^+$ to N_2 gas had to be modified considerably to ensure collection of samples with low air contamination. It was found that added N does not become uniformly diluted with the total soil N. Evidence was found of an "active" soil N fraction composed essentially of amino acids and acid-soluble humin. A portion of the tagged N which was added became initially immobilized in this "active

fraction", but was subsequently released by mineralization and appeared to enter the inorganic pool of soil N. There was an inverse relationship between the inorganic fraction of soil N and the aforementioned "active" fraction.

There was evidence that the Maleb soil was superior to the Cooking Lake from the standpoint of absolute size of the active fraction. Furthermore, the Cooking Lake soil appeared to immobilize a greater portion of the added N in difficultly available form. Fluctuations in the magnitude of the "active" fraction of soil N were reflected in the efficiency of utilization of added N as indicated by the size of the active pool and ultimately in the relative amounts of N taken up from each soil.

$\text{N}^{15}\text{H}_4\text{NO}_3$ was also used to study the phenomenon of NH_4^+ retention in the major horizons of both soils. The Maleb A appeared to have a greater affinity for the NH_4^+ ion than did the Cooking Lake A horizon. In the case of the C horizons the reverse was observed.

Despite the percolation of nine inches of water through the soil columns 48 per cent of added N^{15} was retained in the top inch of the Maleb A horizon and 25 per cent in the Cooking Lake A. This could have important implications under field conditions if nitrogenous fertilizers are applied in NH_4^+ form.

Substantial amounts of added N^{15} appeared to be retained and held in difficultly available form or lost from the Maleb and Cooking Lake C horizons.

The prime reason for the observed difference in N utilization and uptake between the soils appeared to be differences in immobilization-mineralization properties but retention phenomena probably had contributory effects.

ACKNOWLEDGEMENTS

Sincere appreciation is extended to Dr. G. R. Webster for his thoughtful guidance and constructive criticism during the course of this study and his help in the preparation of the manuscript.

Thanks are also extended to Dr. J. A. Toogood, Head of the Department of Soil Science, for his encouragement and to members of his staff for their assistance from time to time.

Gratitude is expressed at this time to Mr. W. E. Bowser of the Canada Department of Agriculture, Soil Survey Section, for his help in selecting the soil samples, and to Dr. J. A. Robertson of the Department of Soil Science and Dr. F. A. Campbell of the Department of Geology for serving on the committee.

The author is also indebted to Dr. H. R. Krouse of the Department of Physics for his invaluable assistance in conducting analyses on the mass spectrometer, to Dr. G. Cumming of the Department of Physics, and Dr. H. Baadsgaard of the Department of Geology for their helpful suggestions in this phase of the study.

Special thanks are extended to Mr. D. H. Lavery for making the facilities of the Agricultural Soil and Feed Testing Laboratory available to the author, to Dr. K. Smillie of the Department of Computing Science for his assistance in the statistical analyses, and to Dr. A. W. Moore of the C.S.I.R.O., Adelaide for initiating the studies on soil N fractionation.

Gratitude is expressed too to Mrs. D. H. Lavery for her efficient typing of the manuscript and to the author's wife, Joana, for her patience, encouragement, and assistance during the tenure of this study.

The author wishes to record his appreciation to the National Research Council of Canada for the financial assistance which made this investigation possible.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
REVIEW OF LITERATURE	3
Nitrogen and Plant Growth.	3
The Nitrogen Cycle	4
Ion Interactions and Their Effect on Nutrient Uptake	5
NH ₄ ⁺ Fixation.	7
Effect of K on the Nitrification of Fixed NH ₄ ⁺	9
Nitrogen-Supplying Power	10
Fate of Added N in Soils	11
Response Surfaces.	13
Mass Spectrometry.	15
Summary of Literature Review	20
HYPOTHESES	22
MATERIALS AND METHODS.	23
Soils Used in Study.	23
Greenhouse Studies	23
Laboratory Procedures.	31
Statistical Analyses	33
Fractionation Studies.	33
NH ₄ ⁺ Retention Studies	35
Mass Spectrometric Analyses.	39
RESULTS AND DISCUSSION	43
Greenhouse Studies	43
Soil Fractionation Studies	93
NH ₄ ⁺ Retention Studies	104
SUMMARY AND CONCLUSIONS.	117
BIBLIOGRAPHY	121
APPENDIX	127

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Classification and Legal Locations of Soils Under Study . . .	24
2. Characterization of Soils Under Study	44
3. Yield of Dry Matter (g.) on Maleb and Cooking Lake A Horizons as a Function of Applied N, K, and Lime	47
4. Analysis of Variance for Yield of Dry Matter on Maleb and Cooking Lake A Horizons	51
5. Analysis of Variance for Yield of Dry Matter on the Individual Soils.	52
6. Yields of Nitrogen (mg./pot) for Specified Nutrient Com- binations Applied to Maleb and Cooking Lake A Horizons. . . .	54
7. Analysis of Variance for Yield of Nitrogen on Maleb and Cooking Lake A Horizons	55
8. Analysis of Variance for Yield of N on the Individual Soils .	57
9. Yields of Potassium (mg.) for Nutrient Combinations Applied to Maleb and Cooking Lake A Horizons.	63
10. Analysis of Variance for Yield of Potassium on Maleb and Cooking Lake A Horizons	65
11. Analysis of Variance for Yield of K on the Individual Soils .	66
12. Yields of Calcium (mg.) for Nutrient Combinations Applied to Maleb and Cooking Lake A Horizons	68
13. Analysis of Variance for Yield of Calcium on Maleb and Cooking Lake A Horizons	69
14. Analysis of Variance for Yield of Ca on the Individual Soils.	70
15. Yield Response (g.) to Nitrogen and Potassium on Maleb and Cooking Lake C Horizons	72
16. Analysis of Variance for Yield of Dry Matter on Maleb and Cooking Lake C Horizons	74
17. Analysis of Variance for Yield of Dry Matter on the Individual Soils.	76
18. Yield of Nitrogen (mg.) on Maleb and Cooking Lake C Horizons as a Function of Applied Nitrogen and Potassium	77
19. Analysis of Variance for Yield of Nitrogen on Maleb and Cooking Lake C Horizons	81

<u>Table</u>	<u>Page</u>
20. Analysis of Variance for Yield of N on the Two Soils.	82
21. Yield of Potassium (mg.) on Maleb and Cooking Lake C Horizons as a Function of Applied Nitrogen and Potassium	83
22. Analysis of Variance for Yield of Potassium on Maleb and Cooking Lake C Horizons	84
23. Analysis of Variance for Yield of K on the Individual Soils .	85
24. Yield of Calcium (mg.) on Maleb and Cooking Lake C Horizons as a Function of Applied Nitrogen and Potassium	88
25. Analysis of Variance for Yield of Calcium on Maleb and Cooking Lake C Horizons	91
26. Analysis of Variance for Yield of Ca on the Individual Soils.	92
27. Total N (me./100 g.) and Atom Per Cent Excess N ¹⁵ in Dif- ferent Fractions of Soil N after Various Periods of Incubation.	95
28. Distribution of N ¹⁵ (me./100 g.) in Different Fractions of Soil N after Various Periods of Incubation.	97
29. Percentages of Added N ¹⁵ Found in Different Fractions of Soil N after Various Incubation Periods	99
30. Average Weight of Soil in Duplicate Columns, 1/3 Atmosphere Per Cent, and Moisture Content at Time of Packing	105
31. Total N (me./100 g.) of Each Soil Segment Following Addition of 20 mg. N ¹⁵ and Leaching.	107
32. N ¹⁵ Content (me./100 g.) of Top Six Soil Segments Following Leaching.	109
33. Per Cent Recovery of Added N ¹⁵ in the Top Six Soil Segments of Each Column.	113

LIST OF PLATES

<u>Plate</u>	<u>Page</u>
1. Morphological Characteristics of Orthic Brown Soil Profile . .	25
2. Morphological Characteristics of Orthic (Thin) Black Soil Profile.	26
3. Morphological Characteristics of Orthic Grey Wooded Soil Profile.	27
4. Arrangement of Columns for NH_4^+ Retention Studies.	37
5. N_2 Gas Converter	40
6. Difference in Growth of Barley on Maleb and Cooking Lake Soils	49

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Analytical Procedure for Fractionation of Soil N	36
2. Yield of N as a Function of Applied N and Lime on Maleb A Horizon (Profile 1).	58
3. Yield of N as a Function of Applied N and Lime on Cooking Lake A Horizon (Profile 1)	59
4. Yield of Dry Matter as a Function of Applied N on Maleb (Profile 1) and Cooking Lake (Profile 1) C horizons.	73
5. Yield of N on Maleb (Profile 1) and Cooking Lake (Profile 1) C Horizons as a Function of Applied N.	78
6. Yield of K on Maleb (Profile 1) and Cooking Lake (Profile 1) C Horizons as a Function of Applied N.	86
7. Yield of Calcium on Maleb (Profile 1) and Cooking Lake (Profile 1) C Horizons as a Function of Applied N.	89
8. Fluctuations of Added N^{15} in the KCl Fraction of Maleb A (Profile 2) and Cooking Lake A (Profile 1) Horizons with Time.	101
9. Fluctuations in N^{15} Content of the Nondistillable Acid-Soluble Fractions of Maleb A (Profile 2) and Cooking Lake A (Profile 1) Horizons with Time	102
10. Distribution of Added N^{15} in Maleb A (Profile 2) and Cooking Lake A (Profile 1) Horizons after Leaching with Water.	110
11. Distribution of Added N^{15} in Maleb C (Profile 2) and Cooking Lake C (Profile 1) Horizons after Leaching	111

LIST OF APPENDIX

<u>Item</u>		<u>Page</u>
1.	Modified Hewitt's Nutrient Solution	127
2.	Mechanical Analysis of Soils under Study.	128
3.	Tube Characteristics of Thermocouple Vacuum Gauge	129
4.	Calibration Curves for Thermocouple Vacuum Gauge.	130
5.	Derivation of Equation for Computing Atom Per Cent N ¹⁵ in a Sample Containing both Nitrogen Isotopes.	131
6.	Calculation of Atom Per Cent N ¹⁵ from Mass Spectrometer Data.	133
7.	Calibration of the Mass Spectrometer for Inherent Discrimination of Mass 28 with Respect to Mass 32	135
8.	Sample Mass Spectrometer Run.	137

INTRODUCTION

The essentiality of nitrogen in the metabolism of growing plants is well-established. Thus, the reserve of plant-available nitrogen as well as the nitrogen supplying power of a soil are factors of singular importance in plant nutrition. A low nitrogen supplying power in a soil may be due to one or more factors. In neutral and alkaline soils for example, toxic nitrite nitrogen may accumulate in levels deleterious to plant growth. Likewise, the fixation of ammonium nitrogen indigenously or otherwise may result in nitrogen unavailability.

On certain soils, plants display symptoms of nitrogen deficiency even after the addition of supposedly adequate amounts of a nitrogen fertilizer. Viets (1961) found that on a non-calcareous, slightly alkaline soil, nitrogen recovery by crops from various nitrogen fertilizers averaged 81 per cent. On a highly calcareous alkaline soil, however, nitrogen recovery averaged only 26 per cent. Viets could not explain the wide disparity in nitrogen recovery, but his experimental results led him to conclude that the difference was not due to the kind of nitrogen fertilizer used. This problem of poor nitrogen recovery from added nitrogen sources as well as low nitrogen supplying power has been reported also by several investigators working on Alberta soils (Synghal et al., 1959; Khan, 1964).

It has also been suggested that ions like potassium may exert an antagonistic influence on the ammonium ion and thus contribute significantly to a shortage of plant-available nitrogen in the soil. Because of the wide range of potassium values in Alberta soils, the effect of potassium on nitrogen availability is considered to be of particular importance. Approximately 3,000 soil samples (0 - 6 inch depth) were analysed for potassium in the Agricultural Soil and Feed Testing Laboratory at the

University of Alberta during the period 1959 to 1961 with 0.025 N HOAc being used as the extractant. A plot of these K values on a map of Alberta revealed that soils from the Brown, Dark Brown, and Thin Black soil zones generally had much higher potassium contents than soils from the Black, Dark Grey, and Grey Wooded zones. Following this, Goettel (1961) determined the forms of potassium in a number of soil series from the Thin Black, Black, and Grey Wooded zones. It was of particular interest that extractions by 1 N NH_4OAc , boiling 1 N HNO_3 and 0.025 N HOAc showed much higher K values for the Airdrie series (Thin Black zone) than for the others studied. It appears reasonable therefore that the effect of K on nitrogen availability in Alberta soils should be established. Since the soils under study also differ in their content of free lime, it was thought that an investigation of the effect of free lime on N uptake might yield useful information. Finally, any study of nitrogen recovery from nitrogen sources added to the soil is concerned directly or indirectly with the ultimate fate of these nitrogen sources after their incorporation in the soil. It seemed logical therefore that an investigation of the transformations and ultimate distribution of the added nitrogen sources in the soils should be included in the study. It was not the intention of the author to compile a nitrogen balance sheet per se. Rather the study was an attempt to investigate some of the factors which might influence nitrogen uptake by plants with a view to determining their relative importance. Essentially then, the broad objective of this investigation was to study the effect of K and free lime on N uptake by plants. Closely allied to this main objective was an attempt to determine the extent and importance of NH_4^+ fixation and nitrogen transformations in the soils under study with a view to elucidating any influence these factors might have on the overall problem.

REVIEW OF LITERATURE

1. NITROGEN AND PLANT GROWTH

Nitrogen is essential for plant growth since it is a constituent of all proteins and hence of all protoplasm. It is generally taken up by plants either as ammonium or nitrate ions, but the absorbed nitrate is rapidly reduced, probably to ammonium form through a molybdenum-containing enzyme. The ammonium ions and some of the carbohydrates synthesized in the leaves are converted to amino acids mainly in the green leaf itself. Nitrogen tends primarily to encourage above-ground vegetative growth and to impart to leaves a deep green colour. With cereals it often increases the plumpness of the grains and the percentage and quality of protein. With all plants it acts as a regulator in that it governs to a considerable degree the utilization of potassium, phosphorus, and other constituents. Moreover, its application tends to produce succulence, a quality particularly desirable in certain crops such as lettuce and radish.

As the nitrogen supply increases in proportion to other nutrients, the extra protein produced allows the plant leaves to grow larger and thus produce a larger available surface for photosynthesis. In fact, according to Russell (1961), over a considerable range of nitrogen supply for many crops, the amount of leaf area available for photosynthesis is roughly proportional to the amount of nitrogen supplied.

Nitrogen also increases the relative proportion of protoplasm to cell wall material. The higher the nitrogen supply the more rapidly the synthesized carbohydrates are converted to proteins and to protoplasm, and the smaller the proportion left available for cell wall material. This latter effect of nitrogen has several consequences. It increases the size

of leaf cells and gives them a thinner wall thus making the leaves more succulent. There is also an accompanying increase in the proportion of water and a decrease in the ratio of calcium to dry matter; the former because protoplasm has more water and the latter because it has less calcium than cell wall material. Excessive amounts of nitrogen produce prolonged vegetative growth in plants, delay maturity, and increase the length of the growing season by keeping the free carbohydrate content of the leaf too low. In addition, it produces such large, thin-walled cells in the leaves that they become very susceptible to attack by insect and fungus pests, as well as to damage by unfavourable weather such as droughts and frost. A very low nitrogen supply, on the other hand, produces leaves with small cells and thick walls and the leaves are consequently harsh and fibrous. Nitrogen deficiency in plant leaves appears generally as a pale-yellow or yellow-green chlorosis depending on the plant species and the extent of the deficiency.

Cereal crops of the temperate regions such as wheat, oats, and barley require only moderate levels of nitrogen. Too high a nitrogen level leads to the production of excessive straw and poor yields of grain. In some cases too the excessive development of straw induces lodging of the cereal grain.

2. THE NITROGEN CYCLE

In all soils there is a considerable intake and outgo of nitrogen during the course of a year and these processes are accompanied by many complex transformations. "This interlocking succession of reactions, reversible, infinitely recurrent and largely biochemical, constitutes the nitrogen cycle" (Russell, 1961).

The nitrogen income of arable soils is derived from crop residues, green manures, farm manure, commercial fertilizers, and small amounts of inorganic N salts brought down by precipitation. In addition, there is the fixation of atmospheric nitrogen accomplished by symbiotic and non-symbiotic micro-organisms. Nitrogen removal from a soil is due to crop usage, drainage losses, erosion, and loss in gaseous forms as elemental nitrogen, nitrous oxide, and perhaps ammonia. Much of the nitrogen added to soil is transformed before removal and organic nitrogen in particular is subject to complex changes. Proteins are converted to various decomposition products; ammonifying organisms convert some of these to ammonium form and nitrifying organisms produce nitrates from the ammonium nitrogen by processes that are still relatively obscure. Thus, a cyclic transfer of nitrogen goes on, abounding with complex transformations and illustrating the remarkable mobility of the element.

3. ION INTERACTIONS AND THEIR EFFECT ON NUTRIENT UPTAKE

Early workers (Bear, 1950) suggested that since an electro-chemical balance must exist in plants, absorption of one ion in excessive amounts by plants would adversely affect the uptake of other ions. There is, however, much that is still obscure about the interplay of different ions in the nutrition of plants and about the mechanisms by which such balances are maintained.

Nielson et al. (1963) studied the effect of ion interactions on the uptake of N, P, Ca, Cl, and S by corn. These workers found that yield increases were obtained as the rates of application of N, P, and K were increased but Cl and S had no effect. There were reductions in content of some of the nutrients, which could be partially explained by a dilution effect resulting from yield increases. Dilution, however, seemed inadequate to

account for the adverse effects of N on per cent K, P on per cent K, K on per cent N, per cent P, and per cent Ca and of Cl on per cent S. In these cases there was strong evidence of the existence of specific antagonisms. There was evidence too of a beneficial effect of one ion on the accumulation of another. For example, increases in content of both P and Ca resulted from increases in application of N. The supply of N appeared to have a dominating influence in the nutrient interactions and there was a highly significant N x K interaction on yield and the uptake of all nutrients under study.

Drake and White (1961), while studying the influence of N on Ca uptake, suggested that N increased the cation exchange ratio of the plant roots. This created a Donnan-distribution which favored Ca uptake. These workers also suggested that this effect may give N an important role in modifying the ratio of K to Ca in some plants.

Walker and Pesek (1963) determined the N, P, and K composition of Kentucky Bluegrass (Poa pratensis) as a function of applied N, P, and K. Using response surfaces to depict the various interactions, these investigators showed that in the absence of applied N, low rates of P and K decreased the nitrogen percentage. At high rates of P and K, however, the N percentage was increased. There was a positive N x K interaction which indicated that the per cent N had increased at a faster rate in the presence of K than could be explained by the linear N effect. There was also an indication that the N concentration in the bluegrass decreased at a slower rate as a result of applied K than could be expected on the basis of the linear K term. When per cent N was expressed as a function of applied K alone, increasing rates of K appeared to decrease the per cent N in the bluegrass, but at a decreasing rate. For example, at a 52 lb./ac. rate of

applied P, added K decreased the plant content of N to a minimum at 35 lb. K/ac. and then increased it. Applied N and K were also found to have statistically significant effects on the uptake of P by the bluegrass.

Plants can, in general, utilize nitrogen both as nitrates or ammonium ions. Following absorption the nitrogen must be reduced in order to facilitate incorporation into the amino acids and proteins so vital to plant growth. Macleod and Carson (1964), working with hydroponic solutions, studied the effect of K on the utilization of NO_3^- and NH_4^+ by alfalfa and orchard grass. These workers found that an increase in potassium supply generally caused a decrease in the total N, protein N, non-protein N, and reduced N in the plant tissue. High rates of nitrogen, unless accompanied by adequate potassium treatment seemed to encourage the accumulation of soluble N products. High potassium levels with low N, on the other hand had detrimental effects on protein content. At low rates of N the NO_3^- content decreased as the rate of K was increased. With higher rates of N, however, the NO_3^- content increased as the rate of K was increased.

4. NH_4^+ FIXATION

Information on NH_4^+ fixation is of practical importance from at least two standpoints. Firstly, as shown by Bower (1950), the use of the neutral N ammonium acetate method for the determination of cation exchange capacity gives low values when applied to soils that fix NH_4^+ under moist conditions. Secondly, the ability of a soil to fix appreciable amounts of NH_4^+ will influence its nitrogen economy. Evidence of NH_4^+ fixation was reported as early as 1917 by McBeth, who was unable to recover from a California soil more than 81 per cent of an added ammonium salt despite prolonged extraction with 10 per cent HCl.

Many soils have the capacity to fix relatively large amounts of ammonium-nitrogen and potassium, especially in their subsurface layers. The mechanism of fixation of the two cations is believed to be similar (Reitemeier, 1951).

Allison et al. (1951), while studying NH_4^+ fixation in clay-loam soils, noted that the fixation of added NH_4^+ increased sixfold when the soils were heated to 100°C as opposed to comparable fixation under moist conditions. Fixation under moist conditions was thought to be due chiefly to illite, while the additional fixation resulting from drying was attributed to both montmorillonite and illite.

Recent reports by a number of workers have indicated substantial percentages of indigenous fixed NH_4^+ in many soils. This suggests that in certain cases mineral nitrogen cannot be justifiably disregarded as being a minute and transient entity. Young (1962), working on C/N ratios in some Pacific Northwest soils, found that the popular concept "that nearly all soil N exists in organic combination" still appears valid for the surface horizons of most mineral soils. It was, however, not adequate for many subsurface horizons as well as for several soils when the entire soil N reservoir was considered. In such cases, Young suggested that a more appropriate generalization would be that "about 80 to 98 per cent of the total N exists in organic combination." Mineral N was found largely as indigenous fixed NH_4^+ but exchangeable NH_4^+ was the dominant mineral form in some of the soils under study.

Hinman (1963) conducted a somewhat similar study on certain Saskatchewan soils. His results added even further emphasis to the importance of fixed ammonium as a portion of inorganic soil nitrogen. He found that the clay fractions of the soils studied were mineralogically

similar, consisting largely of montmorillonite and illite, and they contained essentially the same amounts of fixed ammonium, approximately 2.4 me. NH_4^+ per 100 g. of clay. Surprisingly, however, he also found substantial amounts of fixed ammonium in the silt fraction of the soils studied. A comparison of several paired surface samples of cultivated and virgin soils revealed that cultivation had reduced the average total nitrogen by one-third. The average amount of fixed ammonium, however, appeared to be unaffected by cultivation.

5. EFFECT OF K ON THE NITRIFICATION OF FIXED NH_4^+

Welch and Scott (1960) observed that added K interferes with the nitrification of fixed NH_4^+ in clay minerals but not with the nitrification of NH_4^+ in the form of $(\text{NH}_4)_2\text{SO}_4$. They concluded, therefore, that the added K had blocked the release of fixed NH_4^+ from the clay minerals.

Allison et al. (1951) found that fixed NH_4^+ in soils and clay minerals is more completely nitrified if the free and exchangeable forms of NH_4^+ are removed by leaching with CaCl_2 rather than with KCl . They attributed this difference in the availability of fixed NH_4^+ to the K ion and its greater contracting effect on the crystal lattice.

Nommik and Jansson, quoted by Welch (1960), studied the effect of added K on the availability of NH_4^+ added to an ammonium fixing soil. When K was added simultaneously with NH_4^+ as opposed to NH_4^+ addition alone, there was less carbon mineralization by heterotrophic micro-organisms and less N uptake by plants. In nitrification experiments, however, Jansson found that the typical release of fixed NH_4^+ between the 15th and 30th days of incubation was not affected by the addition of K.

Axley and Legg (1960) observed that plant uptake of N from $(\text{NH}_4)_2\text{SO}_4$ or urea was not greatly affected by the capacity of the soil to fix ammonium unless sufficient K was present to block the release of NH_4^+ . Addition of K with NaNO_3 had little effect on yields or N uptake, but with an ammonium source of N, similar K treatments severely decreased N uptake from soils having appreciable fixation capacities.

6. NITROGEN-SUPPLYING POWER

Considerable effort has been expended to find a procedure for estimating the nitrogen-supplying power of soils, and various biological and chemical methods have been proposed. Most of these are, however, too time-consuming or unreliable for general use. Perhaps the most widely used method is the nitrate accumulation test, but even this procedure has not achieved universal acceptance. The bulk of soil N is thought to be combined in organic substances that are highly resistant to decomposition, but as much as a third of the nitrogen in some soils is in protein form and may be liberated by acid or alkaline hydrolysis (Kojima, 1947; Rendig, 1951). Since only traces of amino acids have been detected in soils (Bremner, 1950), it seems reasonable to assume that proteins are the basic source of soil N released by microbial decomposition. Most of the protein N in soils has lost its original identity as a result of refabrication by soil microbes. This is substantiated by Bremner who found the amino acid composition of the protein fraction from 10 soils to be remarkably constant. Davidson et al. (1951) reported only minor variations in the composition of proteins from podzol and prairie soils. On the basis of these findings Purvis and Leo (1961) subsequently developed a technique for determining the more readily hydrolyzable N fraction in soils and obtained a very high correlation between this value,

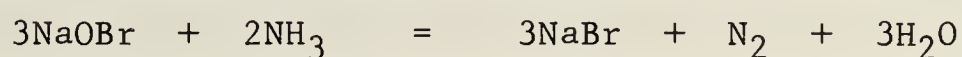
N uptake by a wheat crop, and crop yield. These latter results suggest this potentially available N, or PAN value, of Purvis and Leo is a measure of the source of soil N utilized by plants. These workers also conducted NO_3^- accumulation studies and they obtained a higher correlation between the PAN value and N uptake and crop yield than between the NO_3^- -N value and the latter two factors. Thus it would appear that the PAN value of Purvis and Leo is at least as reliable as, and may even be superior to, the NO_3^- -N value as an index of the nitrogen-supplying power of soils.

7. FATE OF ADDED N IN SOILS

Inorganic nitrogen fertilizers are usually considered to have relatively little residual effect when applied to soils. On the other hand it is a well-known fact that fertilizer N is by no means completely utilized by crops. A certain portion remains in the soil while some may be lost completely. Although the processes which affect the nitrogen not utilized by crops are fairly well understood, investigators have experienced great difficulty in compiling a balance sheet for this N and in estimating its value for future crops. Jansson (1958) in long term pot experiments consistently obtained a 50 per cent crop recovery of tagged fertilizer N in the first year after addition of the nitrogen. In all subsequent years the per cent N recovery approximated 1 per cent.

Little information is available at present on the transformations and distribution of added N in soils. The advent of isotopic tracing techniques involving the use of N^{15} as a tracer has facilitated the differentiation of added N from native soil N. The type of chemical methods for separating and analyzing various nitrogenous components in soils, which can be adopted or modified to incorporate the tracing technique is limited. In general, the amount of nitrogen isotopes in a given medium is determined by

analyzing the N gas liberated from it. The procedure developed by Rittenberg (1946) with slight modifications is still widely used today. Essentially, the procedure involves three principal steps, namely: (a) liberation of N as NH_4^+ by various chemical methods, (b) conversion of the NH_4^+ liberated to gaseous N_2 by alkaline hypobromite oxidation in an evacuated system, and (c) measurement of the isotopic composition of the nitrogen gas with a mass spectrometer. The conversion of NH_4^+ to N_2 gas may be represented by the equation:



Hausman (1899) and Van Slyke (1911) were among the first investigators to develop procedures for fractionating soil N. These procedures consisted largely of a characterization of the various chemical groups in protein, and were based on the premise that soil organic matter is to a great extent proteinaceous. More recently, investigators (Bremner, 1949; Kojima, 1947; Rendig, 1951) have employed modifications of the basic schemes of Hausmann and Van Slyke to analyze soil organic nitrogen. Fractions isolated included hydrolyzed NH_4^+ , amino N, non-amino N, humin N, unhydrolyzed N, amino sugars, and fixed NH_4^+ .

Cheng and Kurtz (1963) using isotopic tracing techniques determined the distribution of added nitrogen among various components of soil nitrogen. The soil N was fractionated into: exchangeable NH_4^+ plus NO_3^- , fixed NH_4^+ , acid hydrolyzable N, and acid-insoluble humin. The acid hydrolyzate was further separated into alkali-labile N which was largely hydrolyzed NH_4^+ plus amino sugars, and alkali stable N which was a composite of amino acid N and acid-soluble, alkali-insoluble humin. Over 90 per cent of the added N in the soils studied was found in the hydrolytic products of soil organic matter, mainly as amino acid N, amino sugar N, and other soluble nitrogen forms.

Stewart et al. (1963) conducted immobilization and mineralization studies on several organic fractions of soil. These workers were mainly concerned with the poor recovery of N fertilizers applied to crop lands. They measured changes in some fractions of soil organic N when straw and fertilizer N were incubated in the soil. Attempts were also made to relate detectable changes in the organic fractions to increases or decreases in inorganic N. Most of the N immobilized during incubation with soil and straw was found in the nondistillable acid-soluble N fraction of the hydrolysate. This fraction was essentially the same as the alkali-stable, acid-soluble fraction of Cheng and Kurtz (1963) and the amino acid fraction of Stevenson (1956). Although the non-distillable acid-soluble fraction constituted only about one-half of the total organic N, studies using N^{15} showed that about three times as much fertilizer N went into this fraction during immobilization as went into the distillable acid-soluble and acid-insoluble fractions combined. These latter two fractions contain hydrolyzed NH_4^+ plus amino sugars and fixed NH_4^+ plus insoluble humin respectively. To a large extent, changes in inorganic nitrogen were accompanied by inverse changes in the nondistillable acid-soluble N fraction. These findings tend to support the hypothesis of Jansson (1958) that added N does not become uniformly diluted with the total N present. There appears to be an active fraction of the total soil N reservoir, and a large portion of immobilized fertilizer N eventually enters this fraction.

8. RESPONSE SURFACES

The importance of experimental design in biological work has been recognized for many years. The traditional design has been to study one factor while holding the others fixed. The most serious shortcoming of such

single factor experiments, however, is that they do not reveal how various factors behave or interact when the levels of other factors are changed. This shortcoming can be overcome by using factorial, composite or similar designs which allow the measurements of interactions. However, it is often difficult to visualize the response pattern, and depicting the results graphically as response surfaces is often helpful. These surfaces, as used in biological work, are geometric models used typically to portray multiple interactions, but they do not alter the physical data. Mathematical models of this type are often used to depict data from very complex experimental designs. In general, for routine agronomic work, a measurement of linear and quadratic effects is adequate to describe a response pattern. At times, however, especially in multi-factor experiments, cubic and even quartic functions must be included in the yield equations. Hader et al. (1957), while investigating yield responses due to Fe and Cu applications, encountered a problem of this nature. Responses appeared to be quadratic at low levels of Cu but at high levels, the yield increased to a maximum, decreased to a minimum, and then increased again. A cubic function was therefore needed to describe the response pattern. Response surfaces may assume various geometric forms varying from relatively simple cubes and octahedra to more complex models for composite designs (Brown, 1956). The geometric model most commonly used in experimentation today may be represented mathematically as follows:

$$Y = B_0 + B_1X_1 + B_2X_2 + B_{11}X_1^2 + B_{22}X_2^2 + B_{12}X_1X_2$$

This represents the estimated yield at any given point on the response surface with X_1 and X_2 the variables in the experiment and the B values the coefficients which can be computed by the method of least squares. Specifically, B_0

represents the yield at the center of the design pattern, B_1 and B_2 coefficients for the linear effects, B_{11} and B_{22} coefficients for the quadratic effects and B_{12} coefficient for the interaction. More complex mathematical equations sometimes incorporate a lack of fit term, which is a measure of the inadequacy of the polynomial equation to describe the data.

9. MASS SPECTROMETRY

1. Theory

Mass spectrometry involves the sorting of ions according to their mass to charge ratio and facilitates the measurement of the isotope abundances of an element. In the gas source instruments used in this study, the neutral molecules are ionized by electron bombardment. These electrons are emitted from a hot filament and accelerated by a potential difference of about 100 volts. The electric field of these electrons removes valence electrons from the neutral molecules or may even decompose the molecules into charged fragments. The ions are then accelerated by a potential of about 2,500 volts through a slit system into the mass spectrometer analyzer tube acquiring kinetic energy given by:

$$\frac{1}{2}mv^2 = eV \quad (\text{Eq. 1})$$

where m = mass of the ion

v = velocity

e = charge of the ion

V = accelerating potential.

In the analyzer tube, the ions are subjected to a magnetic field, where they experience a force at right angles to the direction of the field and the direction of motion. This causes them to move in a circular path.

The magnetic force Bev gives the ions a centripetal acceleration $\frac{v^2}{r}$ and by Newton's second law of motion:

$$Bev = \frac{mv^2}{r} \quad (\text{Eq. 2})$$

where B = the magnetic flux density

r = the radius of curvature of the ion path.

Combining equations 1 and 2 produces the expression:

$$\frac{m}{e} = \frac{B^2 r^2}{2V} \quad (\text{Eq. 3})$$

which holds for the specific mass spectrometers used in this investigation. For any given values of V and B only particles with a certain ratio of m/e would impinge on the collector. Either the voltage V , or the magnetic flux density B , could be varied in order to cause particles with other m/e ratios to fall on the collector.

2. Calculation of N^{15} Content

In the concentration range of 5 to 95 atom per cent N^{15} the three peaks at masses 28, 29, and 30 can be measured with some precision. It is then possible in such cases to calculate the isotopic ratio by a direct comparison of the mass 28 and mass 30 peaks. At lower concentrations of N^{15} , however, it is more convenient and accurate to determine the isotopic ratio by comparing the mass 28 and mass 29 peaks and employing a conversion factor (Appendix 6 and 7). In the present study the latter method was employed, because there were several samples which had an N^{15} enrichment below the critical range. Calculations of N^{15} content based on the mass 30 peak were therefore made solely for the purpose of providing a check on the procedure used and on the efficiency of the mass spectrometer.

Since a small amount of air is normally present in the sample of gas, this must be determined and an appropriate correction applied. The two

most common methods of determining the air contribution to the sample involve the measurement of the argon peak at mass 40 or the oxygen peak at mass 32. From previous calibration of the mass spectrometer with air, the height of the peak at mass 29 due to air contamination can be calculated. Assuming that the extraneous air contained nitrogen with a normal isotopic abundance, the height of the contaminating peak at mass 28 can then be calculated.

If x and y are the respective ion currents at masses 28 and 29 due to contaminating air and i_{28} and i_{29} the observed ion currents, then the true ion current ratio is given by $R = (i_{28} - x)/(i_{29} - y)$. The N^{15} abundance, a_s , of the sample is given by the equation:

$$a_s = 100 / (2R + 1) \text{ atom \% } N^{15}$$

The derivation of this equation is given in Appendix 5. The enrichment, E , of the sample is found by subtracting the natural isotopic abundance a_A as given by Rankama (1954) from that found in the sample, i.e.:

$$E = a_s - a_A \text{ atom \% excess } N^{15}$$

This, however, presents a merely qualitative picture of the transformations being traced. Jansson (1958) combined the N^{15} excess values with data from total nitrogen contents to provide more meaningful quantitative measurements. The tracer level C in each sample was given by:

$$C = N_T E / 100 W \text{ (me.) } N^{15} \text{ excess per gram}$$

where N_T = the total N (me.)

W = the sample weight (g.)

E = the atom per cent excess N^{15} .

3. Sources of Error in N¹⁵ Analysis

(a) Instrumental errors

Determinations of N¹⁵ are subject to several sources of error. Instrumental errors which could arise include lack of reproducibility in potentiometer readings, isotopic fractionation at the inlet leak in the ion source, and background variations. These are generally too small to influence the results significantly.

(b) Memory effects

A small carry-over of labelled N from previous samples may occur during the concentration of Kjeldahl distillates if this is done by re-distillation. Martin et al. (1963) detected a contamination amounting to 0.05 - 0.15 per cent of the tracer present. Memory effects in the mass spectrometer itself are generally negligible.

(c) Reference standard and background contributions

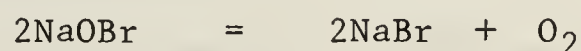
Free or combined natural sources of nitrogen contain an approximately constant fraction of the heavy isotope. The use of N¹⁵ as a tracer requires the correct determination of N¹⁵ in excess of the natural abundance. Hence, incorrect values of this natural abundance could introduce quite substantial errors in the case of small samples. In the light of variations in natural abundance reported by certain workers (Hoering, 1955), it appears that the best procedure is to make a determination of the isotopic ratio in a selected reference standard on the instrument to be used in the study. Compressed nitrogen as well as ordinary air have been used as references. Soloway (1951) and Crable and Kerr (1957) suggested that ordinary air is unsuitable as a reference since the presence of oxygen causes an increase in the mass 28 peak due to production of carbon monoxide in the ion source. This also tends to shorten the life of the filament. On account of these considerations,

Martin et al. (1963) suggested the use of deoxygenated air as a standard.

To determine the absolute values of isotopic abundance, the contribution of background peaks must be accurately known. Calculations of the natural abundance of N^{15} have shown that the values obtained were inversely related to sample pressure. As large a gas volume as practicable is therefore generally used. Then by adjusting the pressure of the reference gas to a value approximating that of the sample, the errors due to background variation, although not eliminated, can be reduced to minimal levels.

(d) Air correction

Although the magnitude of the argon peak at mass 40 has been used by some workers (Holt and Hughes, 1955; Capindale and Tomlin, 1957; Huser, Habfast and Bradke, 1960) to correct for air contamination, there are others (Rittenberg, 1948; Sims and Cocking, 1958) who preferred the oxygen peak at mass 32. The argument of the latter workers is that the oxygen concentration in air is of the same order of magnitude as that of nitrogen; hence, the contaminating peaks at masses 28 and 29 can be calculated with greater precision than from argon measurements. On the other hand, oxygen measurements are subject to error according to Rittenberg (1948) because fresh hypobromite can evolve oxygen, especially in the presence of cupric ions. The decomposition is given by the equation:



Sims and Cocking (1958) found that the decomposition is prevented by the addition of 0.1 per cent potassium iodide to the hypobromite reagent, since it presumably forms a complex with the copper catalyst.

Martin et al. (1963) pointed out another complication in that the composition of dissolved air is somewhat different from that of ordinary air, argon being slightly more soluble than oxygen which in turn is about twice

as soluble as nitrogen. It is impossible to distinguish in the mass spectrometer between contaminating air that has been previously dissolved and that resulting from a leak. The only way out of this dilemma appears to be a reduction of air contamination to negligible proportions.

(e) Contamination by impurities other than air

It is important to ensure, before conversion to N_2 gas, that the ammonium solution is free from organic substances many of which show peaks at masses 28 and 29. Ethanol and methylamine are two such organic compounds. For precise work, the ammonium solutions should be evaporated to dryness in an ammonia-free atmosphere or vigorously boiled before further treatment. Following gas conversion, the use of alcohol-dry ice and liquid air traps has helped greatly in sample purification.

10. SUMMARY OF LITERATURE REVIEW

The following is a summary of the more salient points in the literature as they pertain to the current study.

1. Nitrogen has an essential role in plant nutrition in that it is an important constituent of protein and indeed of all protoplasm. However, the application of either too little or too much nitrogen can have deleterious effects.
2. The exact nature of the interplay of different ions in the nutrition of plants is still comparatively obscure. Very little is known too about the mechanisms in the plant by which ionic balances are maintained.
3. Specific ion interactions have been observed by different investigators and various theories have been advanced in attempts to elucidate the underlying mechanisms.
4. Many soils have the capacity to fix relatively large amounts of ammonium nitrogen as well as potassium, especially in their subsurface layers.

The mechanism of fixation is believed to be the same for both ions and the site of fixation is within the crystal lattices of clay minerals.

5. Two types of NH_4^+ fixation have been reported: one, which occurs under moist conditions, was thought to be due chiefly to illite; the other, which results from drying, was attributed to both montmorillonite and illite.
6. Recent reports have indicated the occurrence of substantial percentages of indigenous fixed NH_4^+ in many soils. This suggests that in certain cases mineral nitrogen might account for a significant portion of the total soil nitrogen reservoir.
7. Investigators have reported that added K interferes with the nitrification of fixed NH_4^+ in clay minerals but not with nitrification of NH_4^+ in the form of an ammonium salt. Several mechanisms have been proposed to explain the exact role played by the potassium ion.
8. Despite exhaustive studies, workers are still searching for an "ideal procedure" for estimating the nitrogen-supplying power of soils. The PAN value of Purvis and Leo appears to be at least as reliable as the standard nitrate nitrogen test as an index of nitrogen-supplying power.
9. Jansson in long term pot experiments consistently obtained a 50 per cent recovery of tagged fertilizer N in the first year after addition of the nitrogen. In all subsequent years, the per cent N recovery approximated 1 per cent.
10. The use of N^{15} as an isotopic tracer has facilitated the differentiation of added N from native soil N. This has made possible a tracing of the transformations which N undergoes when added to the soil. The alliance of isotopic tracing techniques and chemical fractionation procedures has enabled investigators to study the fate of added N in soils with greater assurance.

11. Added N does not become uniformly diluted with the entire soil N reservoir. There appears to be an "active fraction" of soil nitrogen and most of the immobilized nitrogen eventually enters this fraction.
12. Response surfaces have become an important tool in the graphical portrayal of experimental data and the study of interaction in multi-factor experiments.

In view of these findings by previous investigators and the light of preliminary investigations conducted by the author, the following hypotheses were set up.

1. Native K as well as applied K will markedly affect the uptake of applied N by plants.
2. Native lime and added lime will directly or indirectly reduce N uptake by plants.
3. Fluctuations in the magnitude of the "active fraction" of soil nitrogen will be reflected in the relative amounts of nitrogen absorbed by plants.

MATERIALS AND METHODS

1. SOILS USED IN STUDY

The selected soils were orthic virgin profiles developed on the same parent material. The parent material was largely mixed glacial till and the areas sampled may be found on the Wainwright and Vermilion sheets (Wyatt et al., 1944). Table 1 gives the soil types used in the study, the soil zones to which they belong, and the legal locations. The entire profile of each soil was sampled, sub-divisions being made on the basis of major horizons. The profile characteristics of the soils are depicted in Plates 1 - 3.

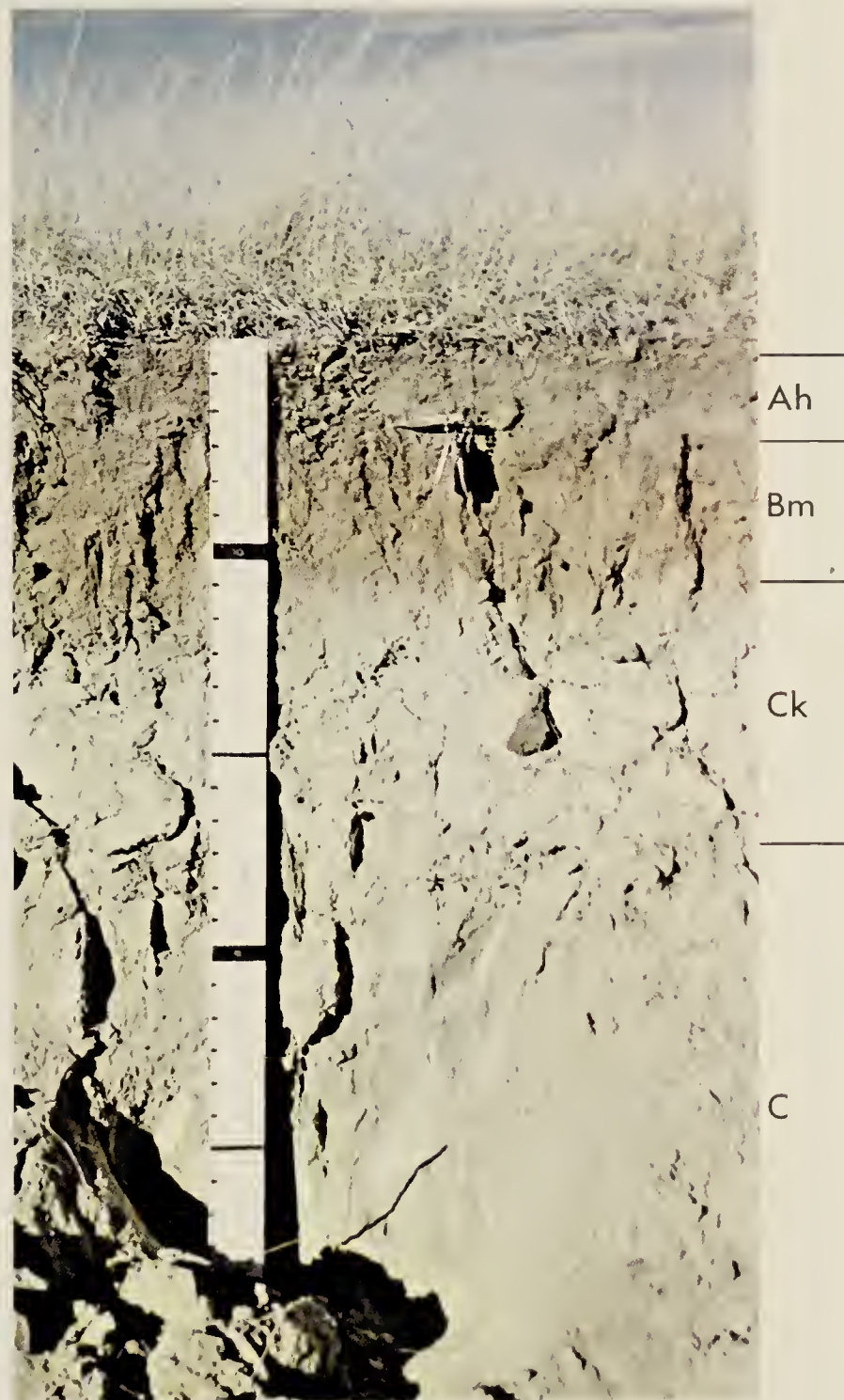
Following sampling, the soils were air-dried rapidly to inhibit nitrification, mixed well and screened through a 2 mm. sieve. Approximately 10 lb. of each soil were taken from the bulk samples for laboratory experiments. The remainder was set aside for growth chamber and greenhouse studies. Prior to use each soil sample was stored in polythene bags and kept in a cool dry location.

2. GREENHOUSE STUDIES

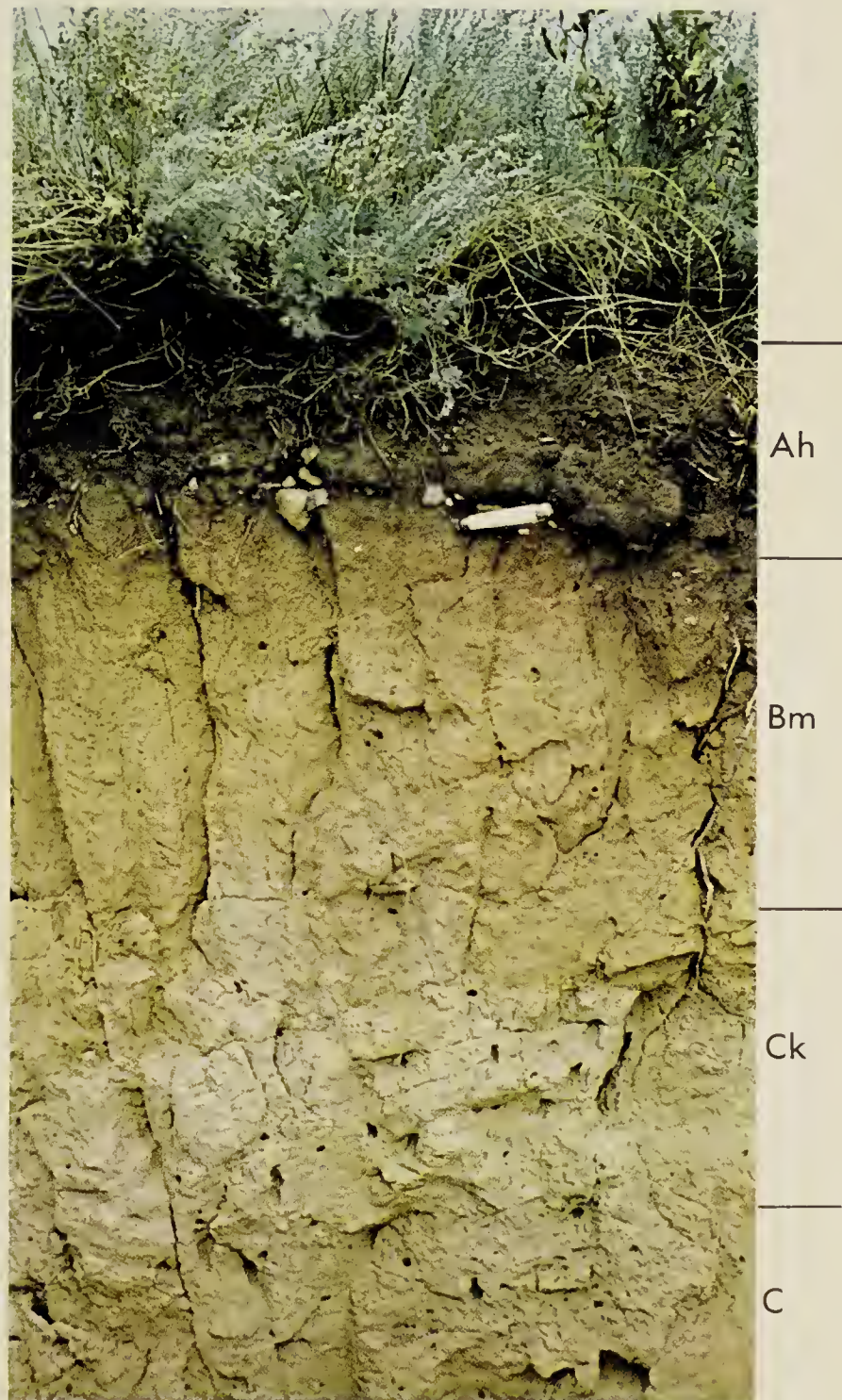
A technique developed by Stanford and Dement (1957) for the study of short term uptake of P by plants was adopted with certain modifications. Essentially, these workers grew plants in sand without added P for approximately 17 days during which time a mat of roots developed at the bottom of the waxed cardboard containers. The exposed root mat with plants intact was then placed in contact with the soil or soil-fertilizer system. The use of P^{32} as an isotopic tracer enabled these workers to detect a measurable uptake of phosphorus during a time span as short as seven days. The great appeal of the method lay in the fact that useful information was obtained

TABLE 1. CLASSIFICATION AND LEGAL LOCATIONS OF SOILS UNDER STUDY

Soil Types	Soil Zones	Parent Material	Legal Locations			
			Qr.	Sec.	Twp.	Rge. W. of
Maleb 1	Brown	Glacial Till	N.W.	14	34	6 4
Maleb 2	"	"	N.E.	25	35	5 4
Maleb 3	"	"	N.E.	6	35	3 4
Elnora 1	Thin Black	"	S.W.	3	48	9 4
Elnora 2	"	"	S.E.	22	48	10 4
Elnora 3	"	"	S.W.	35	49	10 4
Cooking Lake 1	Grey Wooded	"	S.W.	27	53	11 4
Cooking Lake 2	"	"	S.E.	3	55	11 4
Cooking Lake 3	"	"	S.W.	4	55	10 4



Orthic Brown



Orthic (thin) Black



Orthic Grey Wooded

without the necessity of resorting to conventional pot tests which require considerable time. Since no isotopic tracer was used in the present study, a longer time span was required before harvesting. There was still considerable saving in terms of space as well as time despite the modifications made.

Round waxed cardboard cartons of 12-ounce capacity with bottoms removed were nested in identical containers with bottoms intact and filled with 680 g. of washed Ottawa sand. Gateway barley (Hordeum vulgare) was the indicator crop used and ten seeds were planted in each pot at a depth of 1/2 inch. The stand was later thinned to 8 plants per carton. Prior to planting, the barley seeds were treated with ethyl-Hg-p-toluene sulphonanilide (Ceresan) at the rate of 0.5 oz. per bushel as a safeguard against root rot.

Fifty ml. of a modified Hewitt's solution (Appendix 1) were added to the sand in each carton. In addition 40 ml. of distilled water were added thus making for a total of 90 ml. of liquid per carton. During the two weeks following seeding each pot received an additional 50 ml. of the modified Hewitt's solution in order to promote vigorous seedling growth. On an acre basis (assuming 2 million pounds per acre plough depth) the 100 ml. of nutrient solution added to each carton provided:

29 lb. K

78 lb. P

25 lb. N

8 lb. Na

23 lb. Ca

99 lb. Mg

Trace amounts of Zn, Fe, B, Cu, and Co.

The moisture content of each carton was adjusted every two days to a predetermined value by the addition of distilled water. The predetermined value was arrived at by taking the sum of the weights of the cardboard cartons,

the 680 g. of sand, the 90 ml. of solution initially added, and the barley seeds.

At the same time that sand was put in the cardboard cartons, 200 g. of soil or soil plus fertilizer were added to other identical cartons. During the time that the barley seedlings were allowed to grow in the sand cultures, these soils were maintained at a moisture content approximating 1/3 atmosphere percentage by bringing the cartons up to weight every two days. They were also stored in the same greenhouse or growth chamber and under the same environmental conditions as the sand cultures. It should be pointed out that the first two experiments were conducted in the growth chamber, but the third was done in the greenhouse when the environment in the growth chamber became unsatisfactory as discussed in detail later. Illumination in the first two experiments was provided by a bank of fluorescent lamps and in the third experiment by a series of 200 watt light bulbs. In all cases the plants were illuminated daily for 16 hr. In order to induce tillering¹ the following temperature sequence was used:

70° F for 7 days

55° F for 13 days

60° F for 14 days

70° F for the remaining time span.

The temperature of the growth chamber was recorded every 5 minutes by an automatic recorder which indicated an average temperature variation of $\pm 2^{\circ}$ from the set value. Temperature control was not as good in the greenhouse and occasional fluctuations of up to 10° above the set value were observed.

Relative humidity was maintained automatically at 50 per cent in the growth chamber but there was no control in the greenhouse.

After 17 days the mat of barley roots in each carton, with the plants still supported by sand, was placed in contact with the soil or soil

¹ Personal correspondence, Dr. L. Johnson, Dept. of Genetics, Univ. of Alberta.

plus fertilizer in the previously prepared cardboard cartons.

The soils used in the growth chamber studies were the A and C horizons of one Maleb profile and the corresponding horizons of one Cooking Lake profile.

For the A horizons the experimental design was a 3 x 3 x 3 factorial replicated twice. The design used for the C horizons was a 3 x 3 factorial replicated three times. The nutrient variables in the first case were nitrogen at levels of 0, 150, and 300 lb./ac., K at levels of 0, 150, and 300 lb./ac., and lime at levels of 0, 5, and 10 tons per acre.

The levels of N and K used for the C horizon pots were the same as those used for the A horizon cartons. No lime was applied to these cartons because the C horizons of these soils were already endowed with an indigenous excess of lime, as was indicated by the vigorous effervescence following HCl treatment.

The choice of 5 and 10 tons as the lime levels in the A horizons was motivated by a desire to provide an excess with the highest lime rate. This would provide a comparison with the excess native lime in the C horizons.

After transfer of the barley seedlings to the soil cultures, each carton was fitted with bamboo stakes and "twist-em" bands to support the young plants. The moisture content of the sand-soil cultures was adjusted every two days to the 1/3 atmosphere percentage by bringing them up to a predetermined weight with distilled water.

The cartons were rotated twice weekly within each sub-block in order to minimize positional effects. Twice during the growing season the plants were sprayed with liquid Derris of concentration 150 ml./3 gal. of water for the control of aphids.

The various nitrogen levels were applied by the addition of the appropriate aliquots from an $(\text{NH}_4)_2\text{SO}_4$ solution of concentration 14.40 g./5 liters. Potassium additions were similarly made by taking aliquots from a KCl solution of concentration 4.76 g./5 liters. Lime was applied by the direct addition of the requisite weights of fine CaCO_3 to each pot.

The plants were harvested at the same stage of physiological development. When 50 per cent of the plants in any given carton had reached the early boot stage, as indicated by a protrusion of the awns, the entire set of eight plants in that carton was harvested. This was done by clipping the plants off at the sand surface. The harvested plant tops were placed in previously weighed paper bags and dried for 24 hr. in a drying oven at 150°F .

Attempts to harvest the plant roots for possible determination of root:top ratios were abandoned because of the difficulty of separating the roots from the sand without significant loss of fine roots.

3. LABORATORY PROCEDURES

1. Preparation of Plant Material

After weighing the dried plant material to determine dry matter yields, it was ground to a size of 20 mesh in a Wiley (intermediate model) laboratory grinding mill and stored in labelled glass containers until analyzed.

2. Digestion of Plant Material

Approximately 0.5 g. of each sample was digested in 5 ml. of boiling concentrated H_2SO_4 on a micro-Kjeldahl digestion unit (Taras, 1958). The catalyst was 0.5 ml. of 10 per cent HgSO_4 , and 0.5 g. of Na_2SO_4 was added to the digestion mixture to increase the boiling temperature of the H_2SO_4 . Ten drops of a 30 per cent solution of H_2O_2 in water were added to each flask at the end of the digestion to clarify the digest, care being taken to cool the

mixture before adding the peroxide and also to boil off the excess peroxide. The H_2SO_4 digest was diluted to 50 ml. with deionized water and appropriate aliquots used for the determination of N, K, and Ca.

3. Nitrogen Determination

A 10 ml. aliquot of the H_2SO_4 digest was transferred directly to a micro-Kjeldahl distillation unit, which had been previously flushed out with steam from a reservoir of boiling demineralized water. Fifteen ml. of a $\text{NaOH-Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution were added and the mixture heated with steam from the aforementioned reservoir until approximately 40 ml. of distillate had collected in a boric acid trap. The entire distillation unit was flushed out with demineralized water between samples. The distillate was then titrated to a grey-purple end point with standard HCl of normality 0.02. The indicator used was a 2:1 mixture of methyl red and methylene blue in ethanol.

4. Potassium Determination

For potassium determinations, a 3 ml. aliquot of the original digest was diluted to 25 ml. with demineralized water. A 10 ml. aliquot of this diluted digest was further diluted to 20 ml. by the addition of 10 ml. of 100 p.p.m. LiNO_3 , which was used as an internal standard. The K content of the extract was then found by analyzing the latter extract on a Baird Atomic Flame Photometer and comparing the values with a predetermined standard curve.

5. Calcium Determination

The calcium content of the extracts was determined by the procedure outlined by Engelhardt (1959). A 10 ml. aliquot of the H_2SO_4 digest was used. To this was added in turn 12 ml. of 8N KOH , and 6 ml. each of KCN and $\text{NH}_2\text{OH} \cdot \text{HCl}$. The mixture was stirred well and then titrated to a blue end

point with 0.01N EDTA, Cal-Red being used as the indicator. The hydroxylamine hydrochloride was used to reduce any Fe and Mn present to the divalent form. The interference of these ions in the titration procedure was prevented by the formation of complexes with the KCN.

4. STATISTICAL ANALYSES

The data for yield of dry matter and nutrients were programmed, and statistical analyses were carried out on an IBM 1620 computer.

5. FRACTIONATION STUDIES

The procedure followed in the soil fractionation was a combination of the methods used by Cheng and Kurtz (1963) and by Stewart et al. (1963). The soils used in the study were the A horizons of one Maleb profile and one Cooking Lake profile. The time spans selected for incubation were 0, 10, 20, 40, and 80 days. For each span 100 g. of each soil were weighed out in triplicate. The moisture content of the samples was adjusted to approximately 1/2 the 1/3 atmosphere percentage by spraying the soil with distilled water on a sheet of wax paper. The samples were then transferred to labelled wide-necked Erlenmeyer flasks of 500 ml. capacity, which had been previously weighed. To each flask excepting those at zero time were added 10 ml. of an $N^{15}H_4NO_3$ solution containing 2 mg. N^{15} per ml. so that 20 mg. of N^{15} were added per 100 g. of soil. Preliminary analyses confirmed that the N^{15} was all in the NH_4^+ form and that the NO_3^- moiety was unlabelled. The moisture content of each sample was then adjusted to the 1/3 atmosphere percentage by bringing the flasks up to a predetermined weight with distilled water. Each flask was then filled with a loose cotton plug and incubated in an oven at 30°C for the indicated time spans. Every two days the moisture content of the samples was readjusted to the 1/3 atmosphere percentage with distilled water.

After each time span the samples were air-dried for 24 hr. The exchangeable NH_4^+ and nitrates were removed by extraction with 1 N KCl for 1/2 hr. The extract was removed by filtration under suction. The residue was predigested with 12 N HCl for 50 hr. and following this the acid was diluted to 6 N with distilled water and the flasks were placed in a constant temperature bath at 95°C for 15 hr. The HCl extract was removed by filtration under suction, and the residue was washed twice with 25 ml. of 0.1 N HCl. The filtrate was diluted to 250 ml. and the residue was air-dried for 24 hr. All fractions were then subjected to Kjeldahl analysis for total organic and ammoniacal nitrogen in accordance with the A.O.A.C. procedure (1955). For convenience this will be referred to as total nitrogen throughout the rest of the study. To each flask was added a "Kel-Pak" containing 9.9 g. K_2SO_4 , 0.08 g. CuSO_4 , and 0.41 g. HgO . K_2S or $\text{Na}_2\text{S}_2\text{O}_3$ was later added in the NaOH to precipitate the Hg. The HCl extract was further subdivided into distillable acid soluble and non-distillable acid soluble fractions by the procedure of Stewart et al. (1963). Essentially, a 100 ml. aliquot of the extract was subjected to alkaline distillation to determine the distillable acid soluble fraction. Considerable foaming was encountered during this distillation and so a cube of paraffin wax was added to each flask as a foam inhibitor and heating was conducted very slowly. A similar 100 ml. aliquot was subjected to normal Kjeldahl digestion followed by alkaline distillation in order to determine the total N content of the extract. The difference in value between the total N of the extract and the distillable acid soluble N gave the amount of non-distillable acid soluble nitrogen present. After distillation all samples were titrated to a pale amber end point with standard 0.1 N H_2SO_4 as the titrant, and a 5:3 Methyl Red-Brom Cresol green solution as the indicator.

To each titrated distillate were then added 3 ml. of 0.1 N H_2SO_4 and the sample was evaporated to a volume of approximately 10 ml. on a sand bath. The concentrated distillates were then stoppered and stored in the dark under refrigerated conditions until subsequent conversion to N_2 gas for mass spectrometric analysis.

A flow chart of the analytical procedure used to fractionate soil N is presented in Fig. 1.

6. NH_4^+ RETENTION STUDIES

A technique used by Chao et al. (1960) in the investigation of sulphate adsorption in soils was adopted with some modifications. Since the labelled N added was all in the form of NH_4^+ nitrogen this study was essentially a comparison of the relative ability of the soils under study to retain the ammonium ion. The A, B, and C horizons of each of two soils, the Maleb and Cooking Lake, were used.

Glass tubing segments of 1.5 in. diameter and 1 and 2 in. lengths were connected with Wendar contact cement and electrical tape. The top of the column was formed by 6 one-inch segments and the lower part by 6 two-inch segments. The entire column was then sprayed with plastic spray paint to provide a water-tight column. The lower end of the column was stoppered by a one-hole #7 rubber stopper containing a piece of glass tubing to which a polythene tube was attached (Plate 4). A thin pad of glass wool was put on top of the rubber stopper to prevent soil from filling the drainage outlet. The tip of the polythene tube was inserted into the mouth of a 200 ml. Erlenmeyer flask, which was then sealed with a cotton plug to reduce loss of leachate by evaporation.

The samples under study were screened through a 2 mm. mesh screen and sprayed with distilled water on a sheet of wax paper until their moisture

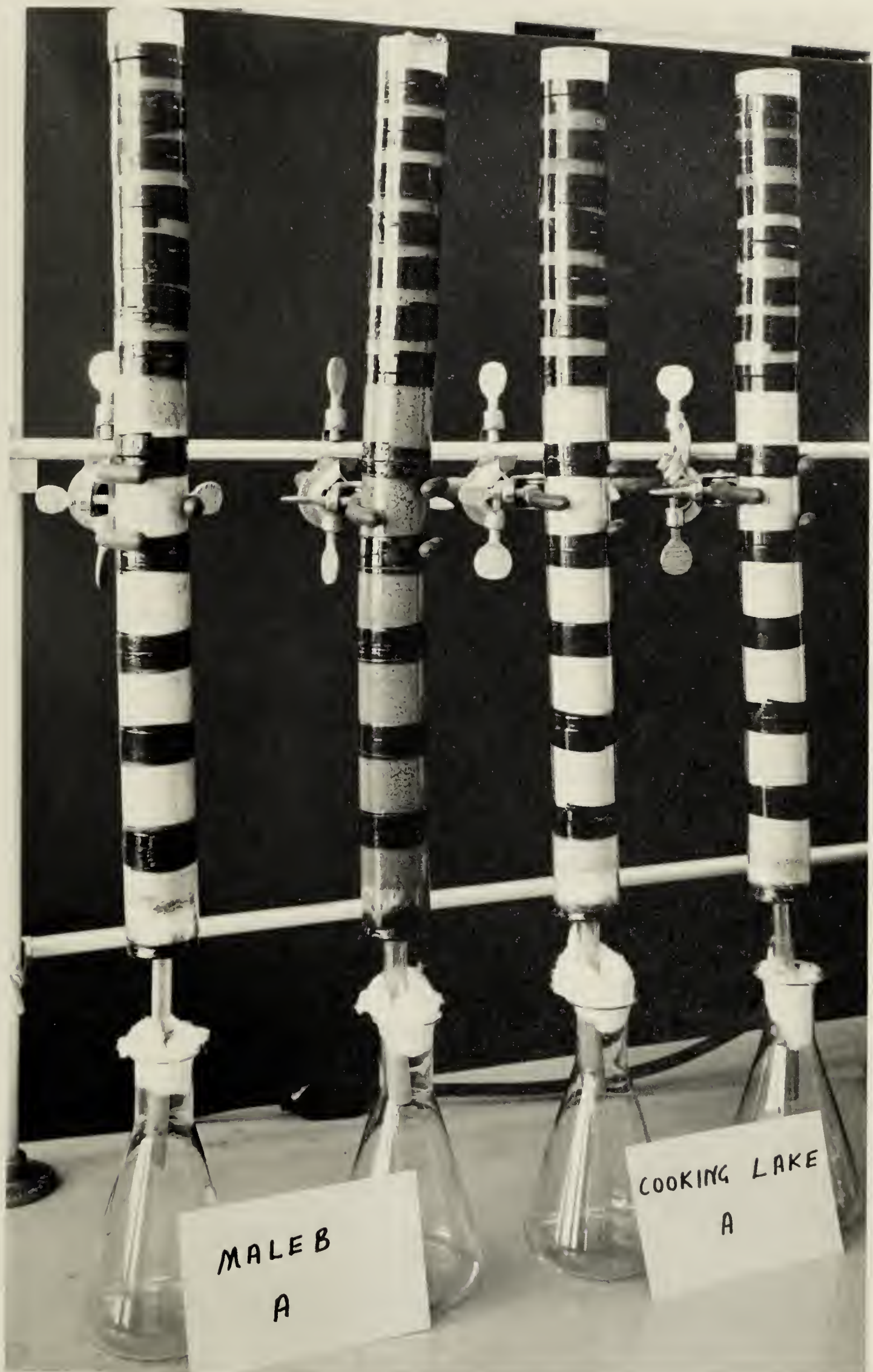
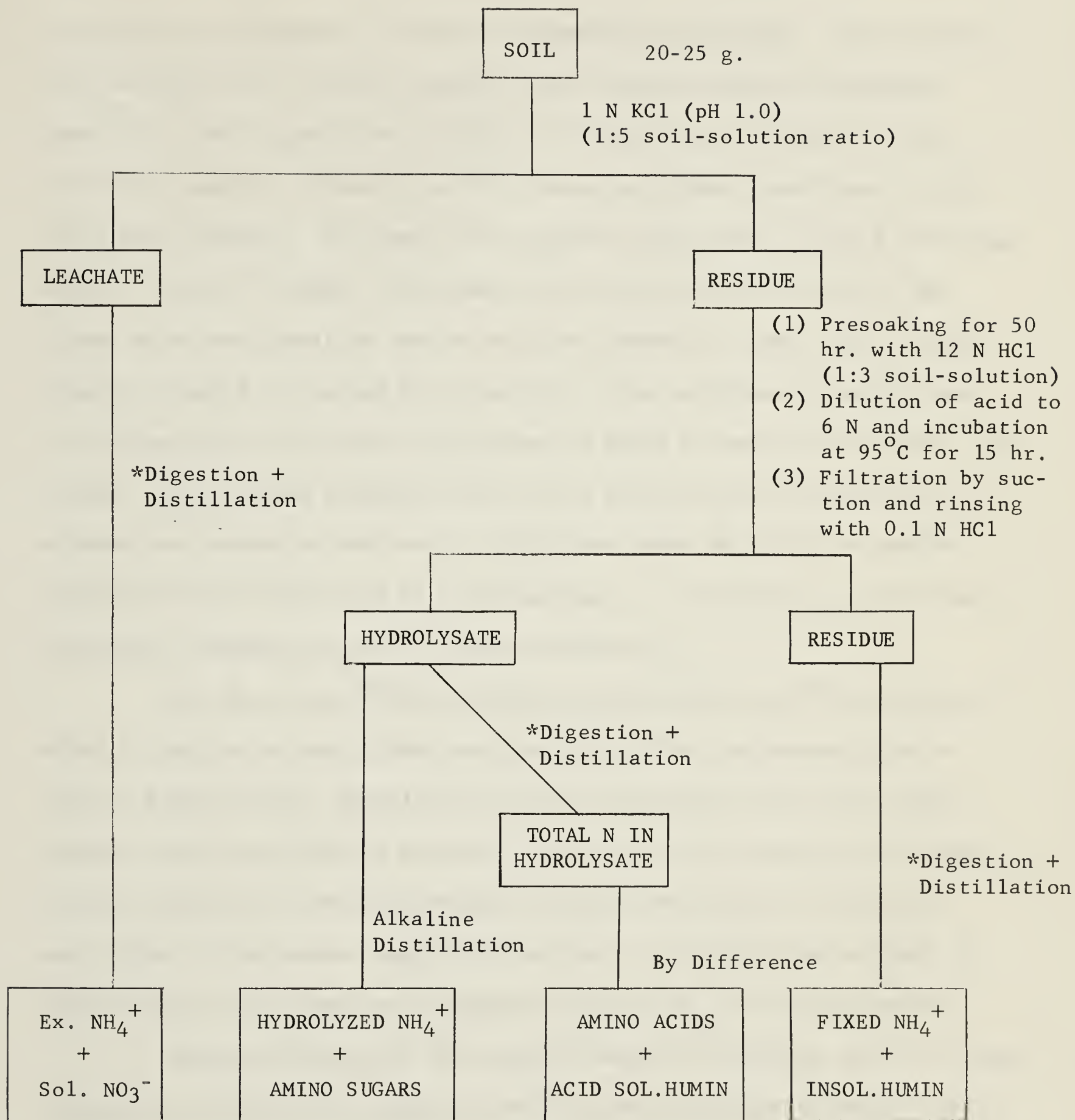


Plate 4. Arrangement of Columns for NH_4^+ Retention Studies



* Kjeldahl digestion + Alkaline distillation with 40% NaOH.

FIGURE 1. Analytical procedure for fractionation of soil N

content was approximately 1/2 the 1/3 atmosphere percentage. The moistened soil was mixed well and then packed in the columns using the following technique: small quantities of each soil sample were introduced to the vertically mounted columns by way of a large polythene funnel with a polythene pipe attached. The funnel was rotated slowly while the soil was being added. A piece of rubber tubing was used to gently tap the side of the column after each addition and the soil was tamped six times with a rubber stopper attached to the end of a glass rod. The operation of packing was so systematized that fairly uniform density might be expected throughout the column. Each column contained soil from a single major horizon and the columns were packed in duplicate. Preliminary work on duplicate samples produced results which were in close agreement. The weight of soil in each column was recorded for use in later calculations.

Ten ml. of an $N^{15}H_4NO_3$ solution containing 2 mg. N^{15} per ml. were added to the top of each column and the soil surface was covered with a disc of filter paper. Distilled water was then added to the top of each column, care being taken to maintain a one-inch head of water at all times. In this connection a one-inch segment of glass was sealed to the top of each column in the manner described previously. The water was allowed to leach through the column until approximately 130 ml. had been collected.

After collection of the required amount of leachate the top of each column was covered with a piece of parafilm and the column allowed to drain for at least 24 hr. The segments were then separated by the application of Wendar adhesive thinner at the joints and the soil in each segment was air-dried separately. Kjeldahl analyses were conducted on the soil in each segment and the distillates were prepared for N_2 gas conversion in the manner previously described.

7. MASS SPECTROMETRIC ANALYSES

1. Preparation of Hypobromite (Rittenberg, 1946)

Two hundred grams of NaOH were dissolved in 300 ml. of distilled water. To half this solution, cooled in an ice bath, were added 60 ml. of bromine with vigorous stirring over a ten minute period. The remaining NaOH solution was then added and the mixture stored in a refrigerator for two days. The copious precipitate of NaBr which developed, was removed by filtration under suction and 0.1 per cent KI was added to the filtrate to prevent catalytic evolution of O_2 from the NaOBr. The fresh hypobromite was then stored in a refrigerator. Prior to use the hypobromite was diluted with an equal volume of distilled water.

2. Sample Preparation

The conversion of the Kjeldahl distillates to N_2 gas was conducted in a specially designed gas converter. Attempts to use the apparatus recommended by Rittenberg (1948) were abandoned because of the difficulty in preparing reproducible samples of the desired purity. Despite considerable time spent with this apparatus and exhaustive manipulations, many of the samples were found to be significantly high in oxygen content. This tended to invalidate the use of the oxygen peak at mass 32 to correct for air contamination of the samples.

The gas converter shown in Plate 5 is a refinement of the original apparatus of Rittenberg (1948). It possesses the superior attributes of being able to produce replicate samples from the same preparation as well as prepare samples of predictable purity. Flask A is the reagent flask and initially holds the NaOBr reactant. Flask B is the reaction flask. C is an ethanol-dry ice trap designed to remove H_2O vapour, CO, and other

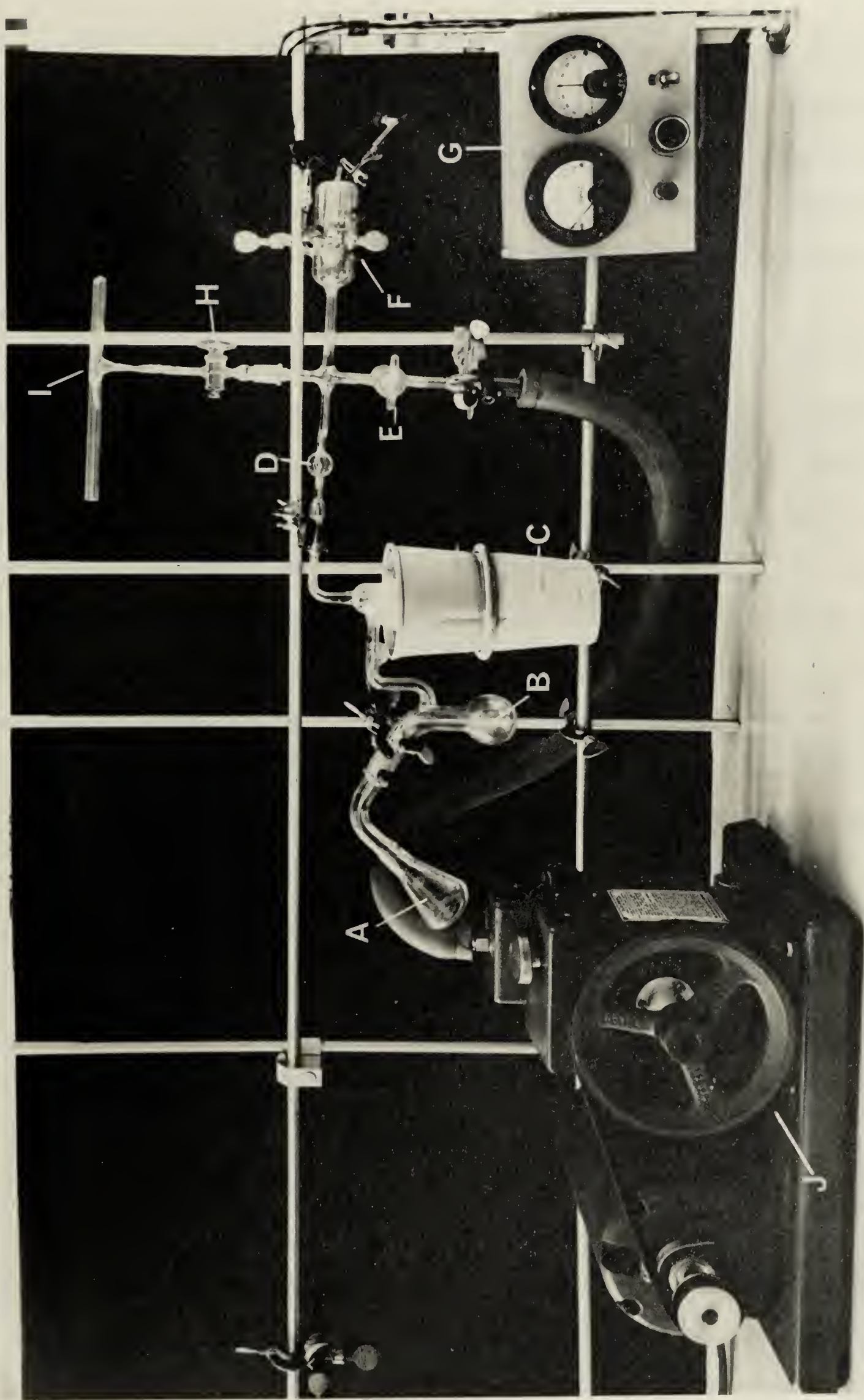


Plate 5. N₂ Gas Converter

impurities. I is a tube fitted with a breakseal and this tube is used to collect the converted N_2 gas. Part F of the apparatus is a thermocouple vacuum gauge which is connected to a voltmeter galvanometer complex G powered by an Eveready dry cell. The vacuum gauge and the two meters were calibrated so that a reading of 20 on the galvanometer corresponded to a vacuum of 10^{-4} mm. Hg approximately.

Two procedures were followed in the preparation of the Kjeldahl distillates for gas conversion. In the first the samples were evaporated to dryness and the residue dissolved in 3 ml. of hot deionized water. In the second procedure the distillates were merely concentrated to a volume of 3-4 ml. instead of being taken to dryness. In both cases, the concentrated sample was boiled vigorously to expel dissolved air and introduced into the reaction flask with a polythene eye-dropper while still hot. Five ml. of diluted hypobromite were added to flask A, the sample tube was fitted as shown and the entire system made airtight by the use of Apiezon (N) high vacuum grease at the joints. The unit was evacuated with the Duo-seal vacuum pump J, and as the pressure fell the liquid in the reaction flask invariably boiled and then froze, while the NaOBr reagent in flask A began to degas. Evacuation was continued until a steady reading of 20 or greater was indicated on the galvanometer with stopcock E shut off. At this time, stopcock D was shut off and flask A rotated in order to introduce the NaOBr into the reaction flask. The mixture was warmed gently to melt the frozen distillate, and the reaction was assumed to be complete when the evolution of bubbles had ceased. With stopcock E to the pump shut-off, stopcock D was now reopened and the N_2 gas allowed to fill the entire system. After a time span of approximately one minute stopcocks D and H were shut off, the sample tube was removed and the collected gas sealed off above stopcock H with an oxy-natural gas flame. The presence of stopcocks D and H facilitated

the collection of duplicate samples from the same preparation.

Two mass spectrometers were used to analyze the nitrogen samples. One instrument was a 6-inch radius 60° Magnetic Analyzer, and was a single collector single inlet type. The second instrument was a 12-inch radius 90° Magnetic Analyzer capable of simultaneous collection of masses 28 and 29. Most of the analyses were done by single collection and the various peaks were traced automatically on a recorder chart.

In simultaneous collection, the current corresponding to mass 28 passed through a calibrated voltage divider and a known fraction was fed inversely to cancel the current corresponding to mass 29. This null or balance point was detected on the recorder and the "fed-back" fraction was read from the voltage divider dial. A magnetic valve system rapidly introduced the unknown sample and a standard alternately into the mass spectrometer. This second instrument was also fitted with mercury reservoirs, which allowed the adjustment of the peak heights to a fairly constant value. With such a system, a precision of 1 part in 10,000 in isotope ratio differences between samples is possible.

Precision on single collection was improved by digitizing the ion current signals with a 5 place integrating digital voltmeter. This eliminates errors in the measurement of peaks on the chart paper. Numbers corresponding to the signal were printed with a digital recorder. Determination of duplicate samples on each instrument after suitable calibration produced results which agreed quite closely.

RESULTS AND DISCUSSION

1. GREENHOUSE STUDIES

Table 2 contains various physical and chemical data of the soils under study. It will be noted that the level of available nitrogen was low in all the soils with the exception of Maleb 2 indicating that nitrification had been effectively arrested by air-drying the samples prior to storage. The conductivity values were all less than 2 millimhos/cm., which suggests that there was no serious salt problem in any of the soils.

The soil reaction of the various A horizons, with the exception of one Maleb profile, ranged from 6.3 - 6.8. Corresponding values for the C horizons ranged from 7.5 for one Cooking Lake soil to 8.2 for the first Maleb profile. It will be further observed that there was an indigenous excess of free lime in all the C horizons with the Cooking Lake C horizons being in general high in free lime and the Maleb and Elnora analogues being very high. There was a marked difference between the three soil types from the standpoint of depth to the C horizon. Whereas the average depth in the Maleb was 14 inches, that in the Elnora was 20 inches and that in the Cooking Lake was over 40 inches. Perhaps the most noteworthy feature of Table 2, however, is the wide range of K values in the soils under study. These values ranged from the relatively low value of 66 lb./ac. for the A horizon of one Cooking Lake profile through the intermediate K values of the Elnora soils to the high value of 452 lb./ac. found in the A horizon of one Maleb profile. This was considered to be a significant factor in view of the desire to study the effect of potassium on nitrogen uptake in these soils.

Since the Maleb and Elnora soils were very similar with respect to the parameters under study, and since they were also quite different from

TABLE 2. CHARACTERIZATION OF SOILS UNDER STUDY*

Samples	Depth (in.)	Available Nutrients			pH	Conductivity millimhos /cm.	p.p.m. SO ₄	Free Lime
		p.p. 2 m.**						
		N	P	K				
Maleb 1A	0- 4	18	42	452	6.7	0.6	--	--
Maleb 1B	4-12	11	10	236	7.1	0.5	--	--
Maleb 1C	12-26	T	--	230	8.2	0.5	--	Very High
Maleb 2A	0- 5	38	28	374	6.8	0.6	--	--
Maleb 2B	5-17	--	23	228	7.4	0.5	--	--
Maleb 2C	17-28	--	T	264	8.1	0.4	--	Very High
Maleb 3A	0- 3	16	13	188	7.7	0.5	--	--
Maleb 3B	3-13	2	9	138	7.1	0.5	--	--
Maleb 3C	13-28	9	16	200	8.0	1.5	150	Very High
Elnora 1A	0- 5	16	18	372	6.7	0.3	--	--
Elnora 1B	5-19	T	14	114	6.4	0.2	--	--
Elnora 1C	> 24	--	--	148	8.2	0.7	--	Very High
Elnora 2A	0- 6	13	25	318	6.4	0.4	--	--
Elnora 2B	6-20	4	5	172	6.1	0.4	--	--
Elnora 2C	20-32	T	3	252	8.0	0.5	--	Very High
Elnora 3A	0- 5	18	14	188	6.7	0.4	--	--
Elnora 3B	5-20	--	T	196	7.6	0.5	--	High
Elnora 3C	20-32	--	--	186	8.2	0.7	--	Very High

(Continued)

TABLE 2. (Continued)

Samples	Depth (in.)	Available Nutrients			pH	Conductivity millimhos/cm.	p.p.m. SO ₄ ⁼	Free Lime
		p.p. 2 m.**						
		N	P	K				
Cooking Lake 1A	0- 8	T	8	88	6.5	0.4	--	--
Cooking Lake 1B	10-32	--	18	54	5.5	0.2	--	--
Cooking Lake 1C	40-50	--	--	54	7.5	0.4	--	Low
Cooking Lake 2A	0- 7	16	50	138	6.5	0.5	--	--
Cooking Lake 2B	7-42	--	--	82	6.2	0.3	--	--
Cooking Lake 2C	50-60	--	--	106	7.7	0.4	--	High
Cooking Lake 3A	0- 6	T	10	66	6.3	0.2	--	--
Cooking Lake 3B	6-32	T	--	58	6.6	0.3	--	--
Cooking Lake 3C	36-48	2	T	62	7.7	0.4	--	High

* Data provided by the Agricultural Soil and Feed Testing Laboratory.

** Parts per 2 million.

the Cooking Lake profiles, it was decided that the remainder of the investigation would be conducted on Maleb and Cooking Lake profiles only. Consequently, with the exception of mechanical analyses (Appendix 2) conducted for the purpose of comparison, no further studies were carried out on the Elnora profiles.

1. A Horizons for Maleb and Cooking Lake

(a) Dry matter yields

Table 3 contains a summary of the yield of dry matter for barley (Hordeum vulgare) grown in soil from the A horizons of Maleb (Profile 1) and Cooking Lake (Profile 1) as a function of applied N, K, and lime. The variety used was Gateway. It might be mentioned that an earlier growth chamber experiment of essentially the same nature but with Olli barley as the indicator crop had been conducted. The young seedlings, however, were lacking in vigor, tended to be chlorotic, and produced a very poor yield of dry matter. In an effort to produce more vigorous vegetative growth and also to provide enough plant material for chemical analysis, the Olli barley was replaced by the Gateway variety and the number of seeds per pot was increased from six to eight. There was one other factor which made it necessary for the first experiment to be repeated. Approximately three weeks after seeding, the tops of nearly all the seedlings displayed symptoms of leaf injury from an undetermined source. The plant roots all appeared to be healthy, but the condition of the tops varied from mild chlorosis and chlorophyll breakdown to acute necrosis of the tips. The plants were also stunted and generally unthrifty. Despite exhaustive examination by the Plant Pathologists no plant disease could be detected. The fact that check plants as well as treated ones were affected in like fashion, ruled out the possibility of toxicity in the nutrient solution. The most plausible

TABLE 3. YIELD OF DRY MATTER (g.) ON MALEB AND COOKING LAKE A HORIZONS
AS A FUNCTION OF APPLIED N, K, AND LIME
(Average of 2 Replications)

N (lb./ac.)	K (lb./ac.)	Lime (T./ac.)					
		0	Av.	5	Av.	10	Av.
<u>Maleb A Horizon (Profile 1)</u>							
0	0	0.87		0.74		0.68	
0	150	0.86	0.84	0.78	0.80	0.69	0.71
0	300	0.78		0.88		0.77	
150	0	0.86		1.02		0.86	
150	150	1.02	0.96	0.83	0.92	0.78	0.85
150	300	1.00		0.90		0.90	
300	0	0.98		1.04		0.80	
300	150	1.32	1.18	0.96	1.02	0.88	0.88
300	300	1.24		1.05		0.96	
<u>Cooking Lake A Horizon (Profile 1)</u>							
0	0	0.48		0.63		0.62	
0	150	0.46	0.49	0.64	0.58	0.74	0.64
0	300	0.54		0.47		0.55	
150	0	0.56		0.68		0.64	
150	150	0.67	0.60	0.46	0.58	0.70	0.71
150	300	0.57		0.60		0.80	
300	0	0.42		0.56		0.51	
300	150	0.44	0.45	0.48	0.55	0.62	0.60
300	300	0.50		0.61		0.66	

explanation is that the plants were damaged by gases detected leaking from the sewer outlet in the floor of the chamber owing to a defect in the exhaust system. In order to eliminate this factor, the experiment was repeated in another growth chamber.

Despite the precautions taken, however, the overall yield of dry-matter was lower on both soils than desired and micro-techniques had to be employed in order to obtain chemical analyses on each sample. It seemed interesting to the author that the plants growing on the Maleb soil were, almost without exception, greener, taller, and more vigorous than the corresponding Cooking Lake analogues. This difference in growth response is indicated by the values shown in Table 3 and portrayed even more vividly in Plate 6.

As mentioned earlier the plants were all harvested at the same stage of physiological development, namely the early boot stage. Owing to the differences in the nutrient combinations applied to each culture, there were differences in the time span required for the plants to mature to the early boot stage. Nevertheless, all plants were harvested within a period of five days and in general the plants on the Maleb soil reached the early boot stage at a later date than the Cooking Lake analogues. Since the Cooking Lake A cultures were also generally lower in their yield of dry matter as well as their yield of N, it is believed that some factor, possibly nutrient interaction, imposed a stress on N uptake, and consequently reduced vegetative growth on this soil. This probably explains the earlier maturity observed. The belief that nutrient interaction was indirectly responsible for the earlier maturity of the Cooking Lake A cultures receives added support when one considers the lime treatments on the Cooking Lake soil. It will be shown later (Table 5) that lime had a beneficial effect on growth on the Cooking



Plate 6. Difference in Growth of Barley on Maleb and Cooking Lake Soils.

Lake soil. It was not surprising therefore that the Cooking Lake A cultures treated with medium to high levels of lime reached the early boot stage of physiological development at approximately the same time as did the majority of the Maleb cultures. There was very little difference in the time required for maturity between the cultures on the Maleb and Cooking Lake C horizons, both of which had an indigenous excess of free lime.

Table 4 contains the statistical analysis of the data presented in Table 3. There was no significant difference between replicates, indicating that the environmental conditions in the chamber were fairly uniform throughout the duration of the experiment. As expected from Table 3 and Plate 6, the difference in growth and yield of dry matter on the two soils was significant at the 1 per cent level. The main effect of applied N was significant at the 1 per cent level but applied K and lime did not appear to affect the yield of dry matter to any significant degree when the data for the two soils were bulked for analysis. The analysis of variance also revealed highly significant N x soil and lime x soil interactions with respect to dry matter yields.

It will be noted that Table 4 provides no information on the effect of each factor on the individual soils. In order to facilitate a closer study of these effects an analysis of variance was conducted for the yield of dry matter on each soil. The results are presented in Table 5. It can be seen from this table that there was no significant difference between replicates on either soil. It is evident also from Table 5 that the highly significant main effect of N observed in Table 4 is almost entirely accounted for by the strong positive yield response to N on the Maleb soil. The main effect of N on the Cooking Lake soil was just below the significance value at the 5 per cent level. One surprising fact revealed by the individual

TABLE 4. ANALYSIS OF VARIANCE FOR YIELD OF DRY MATTER ON MALEB
AND COOKING LAKE A HORIZONS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
Replicates	1	0.016	0.016	0.826
N	2	0.230	0.115	5.887**
K	2	0.037	0.018	0.944
Lime	2	0.011	0.006	0.284
Soil	1	2.920	2.920	149.486**
N x K	4	0.069	0.017	0.881
N x Lime	4	0.038	0.009	0.485
K x Lime	4	0.122	0.030	1.560
N x Soil	2	0.381	0.190	9.749**
K x Soil	2	0.009	0.005	0.235
Lime x Soil	2	0.433	0.216	11.074**
N x K x Lime	8	0.092	0.012	0.592
N x K x Soil	4	0.032	0.008	0.403
N x Lime x Soil	4	0.053	0.013	0.680
K x Lime x Soil	4	0.042	0.010	0.538
N x K x Lime x Soil	8	0.093	0.012	0.596
Error	53	1.035	0.020	
Total	107	5.615		

** Denotes significance at the 1% level.

TABLE 5. ANALYSIS OF VARIANCE FOR YIELD OF DRY MATTER ON
THE INDIVIDUAL SOILS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
<u>Maleb A Horizon (Profile 1)</u>				
Replicates	1	0.057	0.057	3.167
N	2	0.528	0.264	14.569**
K	2	0.041	0.021	1.143
Lime	2	0.290	0.145	8.008**
N x K	4	0.040	0.010	0.552
N x Lime	4	0.067	0.017	0.921
K x Lime	4	0.098	0.024	1.353
N x K x Lime	8	0.095	0.012	0.654
Error	26	0.471	0.018	
Total	53	1.688		
<u>Cooking Lake A Horizon (Profile 1)</u>				
Replicates	1	0.018	0.018	1.354
N	2	0.083	0.041	3.104
K	2	0.005	0.002	0.176
Lime	2	0.153	0.077	5.748**
N x K	4	0.060	0.015	1.131
N x Lime	4	0.024	0.006	0.456
K x Lime	4	0.066	0.016	1.235
N x K x Lime	8	0.091	0.011	0.853
Error	26	0.347	0.013	
Total	53	1.006		

analyses of variance was the highly significant main effect of lime on both soils. This effect was not indicated by the gross analysis in Table 4 although there was evidence of a highly significant lime x soil interaction.

(b) Nitrogen yields

Table 6 contains the yields of nitrogen for the combinations of N, K, and lime applied to Maleb and Cooking Lake A horizons. The reporting of the data as yield of N in preference to per cent N or p.p.m. was motivated by a desire to minimize dilution effects, which often arise when yields are markedly different. It will be noted that with only one exception the yields of nitrogen on the Maleb soil were higher than the corresponding values on the Cooking Lake soil. There was a general increase in yield of nitrogen on both soils as the level of applied nitrogen was increased. Conversely, there was a decrease in yield of nitrogen on the Maleb soil as the level of applied lime was increased. On the Cooking Lake soil, lime had a peculiar effect on N levels. The N percentages (not shown) were decreased drastically by the 5 T./ac. application of lime at all three levels of N. The percentages of N were higher for the 10 T./ac. rate than for the 5 T./ac. but still substantially lower than for the zero level of lime. An explanation cannot be given for the peculiar pattern but the need for more study is indicated. These percentages are reflected in the nitrogen yields (Table 6).

The analysis of variance for the data in Table 6 is reported in Table 7. The replicates were not significantly different from each other, which again suggests fairly uniform environmental conditions throughout the growth chamber. Applied N had a highly significant main effect on the yield of N, and this effect appeared to be more marked on the Maleb soil than on the Cooking Lake soil. Applied lime, too, had a marked effect on yield of N but the effect of applied K was not significant on these soils. As indicated

TABLE 6. YIELDS OF NITROGEN (mg./pot) FOR SPECIFIED NUTRIENT COMBINATIONS
APPLIED TO MALEB AND COOKING LAKE A HORIZONS
(Average of 2 Replications)

N (lb./ac.)	K (lb./ac.)	Lime (T./ac.)					
		0	Av.	5	Av.	10	Av.
<u>Maleb A Horizon (Profile 1)</u>							
0	0	14.08		11.96		11.54	
0	150	14.60	13.93	13.52	12.79	10.16	11.36
0	300	13.12		12.88		12.39	
150	0	17.34		17.98		14.52	
150	150	21.26	19.18	13.70	15.88	14.40	14.79
150	300	18.95		15.96		15.46	
300	0	23.01		20.22		16.68	
300	150	27.06	25.54	19.53	20.11	18.12	17.38
300	300	26.55		20.58		17.33	
<u>Cooking Lake A Horizon (Profile 1)</u>							
0	0	8.53		8.99		10.12	
0	150	7.73	8.75	10.08	8.80	13.59	10.72
0	300	9.98		7.32		8.45	
150	0	11.51		11.82		13.26	
150	150	14.64	12.71	6.64	9.53	10.96	12.61
150	300	12.00		10.12		13.62	
300	0	10.68		10.00		9.86	
300	150	11.51	12.02	8.34	9.52	9.86	10.00
300	300	13.86		10.23		10.29	

TABLE 7. ANALYSIS OF VARIANCE FOR YIELD OF NITROGEN ON MALEB
AND COOKING LAKE A HORIZONS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
Replicates	1	1.123	1.123	0.150
N	2	410.471	205.235	27.435**
K	2	2.728	1.364	0.182
Lime	2	157.830	78.915	10.549**
Soil	1	1,056.188	1,056.188	141.189**
N x K	4	19.603	4.901	0.655
N x Lime	4	81.817	20.454	2.734*
K x Lime	4	37.200	9.300	1.243
N x Soil	2	256.113	128.056	17.118**
K x Soil	2	2.513	1.256	0.167
Lime x Soil	2	119.198	59.599	7.967**
N x K x Lime	8	60.569	7.571	1.012
N x K x Soil	4	11.893	2.973	0.397
N x Lime x Soil	4	6.609	1.652	0.220
K x Lime x Soil	4	10.044	2.511	0.335
N x K x Lime x Soil	8	26.558	3.320	0.443
Error	53	396.475	7.481	
Total	107	2,656.932		

* Denotes significance at the 5% level.

** Denotes significance at the 1% level.

in Table 6 the two soils were quite different with respect to the yield of N by the indicator crop. Table 7 reveals that the difference between soils was significant at the 1 per cent level. The N x lime interaction was significant at the 5 per cent level, and there were marked N x soil and lime x soil interactions significant at the 1 per cent level. There were no significant interactions involving K and the effect of multiple interactions involving three or more of the factors under study appeared to be quite small.

Table 8 contains the analysis of variance for yield of N on the individual soils. There was a significant difference between replicates on the Maleb soil but not on the Cooking Lake soil. The highly significant main effects of N and lime reported in Table 7 appear to be mainly due to the strong influence of these factors on the Maleb soil. Table 8 indicates that there were no significant main effects or interactions operative on the Cooking Lake soil although the F values for N and lime main effects were fairly close to significance at the 5 per cent level.

In order to facilitate a closer scrutiny of the various interactions affecting the yield of N, the data in Table 6 were portrayed as response surfaces. These geometrical models are presented in Fig. 2 and 3. It will be recalled from Tables 7 and 8 that K, at the three levels did not have a significant effect on the yield of N. For simplicity, therefore, the three levels of K were averaged for each level of N and each level of lime and these are depicted in Fig. 2 and 3.

Fig. 2 relates the yield of N to applied N and lime on the Maleb A horizon (Profile 1). The yield of N at the zero level of N is represented by the edge of the surface directly above the lime axis. It will be noted that as the level of lime increases the yield of N decreases. The rate of decrease at this zero level of N was fairly uniform throughout as indicated

TABLE 8. ANALYSIS OF VARIANCE FOR YIELD OF N ON
THE INDIVIDUAL SOILS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
<u>Maleb A Horizon (Profile 1)</u>				
Replicates	1	41.134	41.134	7.482*
N	2	623.069	311.535	56.659**
K	2	4.522	2.261	0.411
Lime	2	235.792	117.896	21.442**
N x K	4	5.816	1.454	0.264
N x Lime	4	53.981	13.495	2.454
K x Lime	4	26.583	6.646	1.209
N x K x Lime	8	30.839	3.855	0.701
Error	26	142.958	5.498	
Total	53	1,164.694		
<u>Cooking Lake A Horizon (Profile 1)</u>				
Replicates	1	24.147	24.147	3.315
N	2	43.517	21.758	2.987
K	2	0.721	0.361	0.050
Lime	2	41.238	20.619	2.831
N x K	4	25.681	6.420	0.881
N x Lime	4	34.448	8.612	1.182
K x Lime	4	20.664	5.166	0.709
N x K x Lime	8	56.284	7.036	0.966
Error	26	189.372	7.284	
Total	53	436.073		

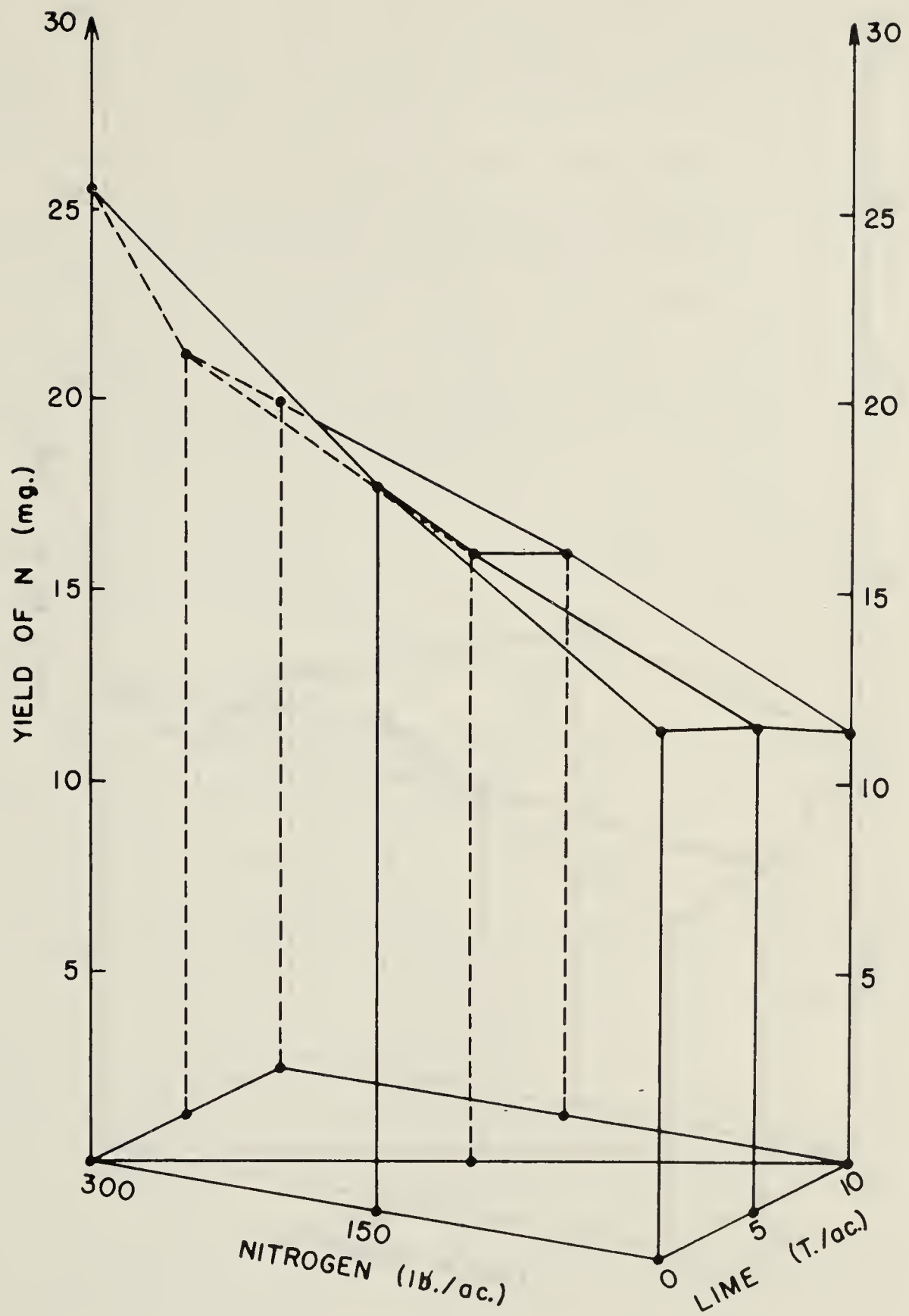


Figure 2. Yield of N as a function of applied N and lime on Maleb A horizon (Profile 1) (Av. of 3 levels of K).

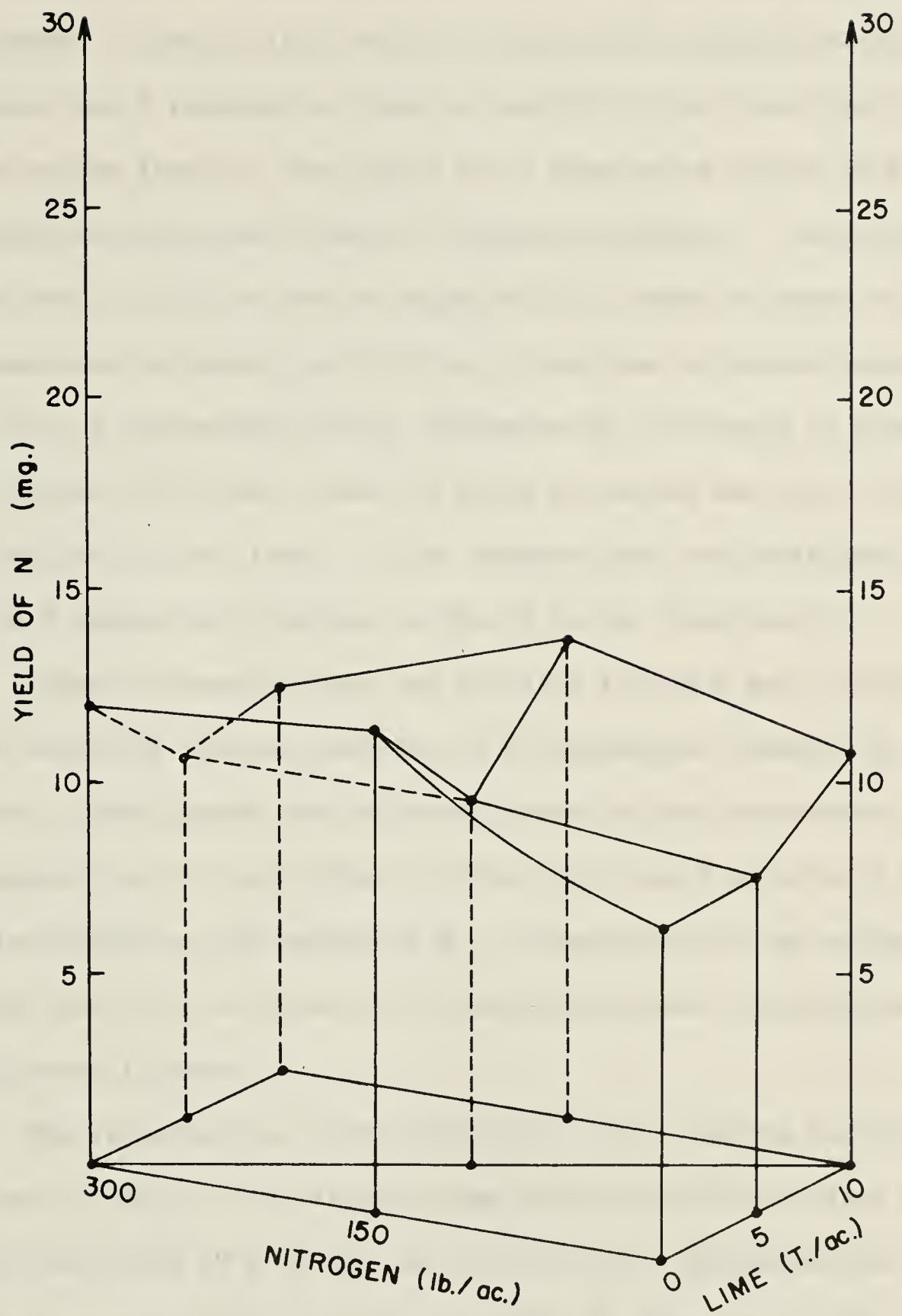


Figure 3. Yield of N as a function of applied N and lime on Cooking Lake A horizon (Profile 1) (Av. of 3 levels of K).

by the fact that the surface edge directly above the lime axis is very nearly linear. A second line over the surface and parallel to the lime axis depicts the N response to lime at the 150 lb./ac. level of N. Increases in the level of lime again had a depressive effect on N uptake but in this case the effect was not uniform throughout. An increase in lime from zero to 5 T./ac. was accompanied by a sharp decrease in N uptake. As the lime rate increased to 10 T./ac., there was a further decrease in N uptake but at a decreasing rate as indicated by the change in slope of the ligand. At the 300 lb./ac. level of N the situation was quite similar to that at the 150 lb./ac. level. It is evident that the inhibitory effect of lime on N uptake was greatest at the 10 T./ac. lime level.

Ligands directly above and parallel to the N axis show that at the three levels of lime an increase in N application resulted in an increase in N uptake. The ligands are all curvilinear in form but differ in slope which suggests that at each level of lime there was a definite N x lime interaction affecting the uptake of N. A comparison of the surface edges at the zero and 10 T./ac. levels of lime reveals that the slope of the two edges is quite different.

The situation was quite different on the Cooking Lake soil as can be seen in Fig. 3. The surface edge directly above the lime axis represents the yield of N at the zero level of N. Increased lime application resulted in increased N uptake. Presumably, the lime application corrected an existing nutrient imbalance, which resulted in increased plant growth (Table 3) and an increase in N uptake. The situation is somewhat different at the 150 and 300 lb./ac. levels of N as can be seen from the two ligands parallel to the lime axis. At the 150 lb./ac. level of N there was an initial decrease in N uptake as the lime level changed from zero to 5 T./ac. Between the 5 and 10 T./ac. lime levels, however, there was a sudden surge

in N uptake, which was almost sufficient to overcome the depressive effect of the 5 T./ac. rate. At the 300 lb./ac. level of N this same general pattern was observed differing only in extent. It appears then that at the intermediate level of lime there was a negative N x lime interaction with respect to N uptake not unlike the situation observed on the Maleb soil. At the high level of lime, however, there was a strong positive N x lime interaction. These interactions make a response surface somewhat resembling a trough with a shallow end at the zero N level and deeper areas at the 150 and 300 lb./ac. levels of N.

The ligands directly above and parallel to the N axis depict the N response at each level of lime. As was the case with the Maleb soil the response pattern was curvilinear in each case. At the zero level of lime, there was increased N uptake as the N level changed from zero to 150 lb./ac. A further increase in N level resulted in a slight decrease in N uptake. At the 5 T./ac. level of lime the 150 lb./ac. rate of N increased uptake by a rather small amount as shown by the slope with no further increase at the 300 lb./ac. rate. At the 10 T./ac. lime level the curvilinear nature of the N response was most marked. In fact between the 150 and 300 lb./ac. N levels there was a marked decrease in N uptake as can be seen from Fig. 3.

It is evident from the foregoing discussion of the two soils that there was no single common effect of applied lime on N uptake but in general it decreased uptake. The influence of lime will vary with different soils and is apparently dependent on the nature of the existing ionic balances among other things.

The absence of a depressive effect of K on N uptake on these soils was contrary to the findings of Walker and Pesek (1963) and McLeod and Carson (1964). The difference could be due to the initial level of K in the soils as well as to the clay mineral composition. No measure of these

factors was reported by Walker and Pesek and so a direct comparison is impossible. The comparison is even more difficult in the case of McLeod and Carson since these investigators worked with hydroponic solutions.

(c) Potassium yields

It will be noted from Table 9 that the yields of K reported for the Maleb soil were considerably higher than the corresponding values for the Cooking Lake soil. This was probably due in part to the fact that the Maleb soil was richly endowed with a reserve of available K some five to six times as great as the comparable value in the Cooking Lake soil (Table 2). It can be seen too from Table 9 that in the case of the Maleb soil, regardless of the level of N and K, an increase in applied lime caused a net depressive effect on K uptake. The trend is quite different on the Cooking Lake soil. Increased lime application at the various N-K combinations tended in this case to increase K uptake. Once again it appears likely that the increased K uptake was partly a reflection of the ameliorating influence of applied lime in correcting an existing nutrient imbalance.

On the Maleb soil, the highest yield of K was in general obtained at the highest level of K application irrespective of the level of the other two nutrients. At any given level of K and lime applied N tended to increase the yield of K. One possible explanation is that the increased N promoted greater vegetative growth of the indicator crop which in turn absorbed K in luxury amounts from the vast available store.

For the Cooking Lake soil there was also a tendency for the highest yields of K to occur at the highest K rates. The influence of levels of N on the yield of K was erratic. There are two factors which accounted, in part at least, for the difference on the two soils. Firstly, the applied N did not produce as vigorous vegetative growth on the Cooking

TABLE 9. YIELDS OF POTASSIUM (mg.) FOR NUTRIENT COMBINATIONS
APPLIED TO MALEB AND COOKING LAKE A HORIZONS
(Average of 2 Replications)

N (lb./ac.)	K (lb./ac.)	Lime (T./ac.)		
		0	5	10
<u>Maleb A Horizon (Profile 1)</u>				
0	0	15.14	12.94	12.54
0	150	15.31	14.52	11.44
0	300	14.30	16.26	14.74
150	0	17.29	17.95	15.51
150	150	19.62	15.82	14.55
150	300	17.50	16.76	17.02
300	0	16.84	19.60	13.40
300	150	24.28	19.51	16.15
300	300	26.38	21.40	17.40
<u>Cooking Lake A horizon (Profile 1)</u>				
0	0	2.76	5.63	4.82
0	150	3.40	7.06	10.32
0	300	4.88	3.95	6.38
150	0	2.75	4.34	6.56
150	150	6.05	4.24	8.27
150	300	4.46	7.26	10.08
300	0	2.06	3.42	4.52
300	150	2.74	3.76	5.48
300	300	5.28	7.60	6.80

Lake soil as it did on the Maleb. This is apparent from Table 3 and was probably due directly or indirectly to a lower availability of the applied N in the Cooking Lake soil. Secondly, there was a lower reserve of available K, from which the crop could draw, in the Cooking Lake soil.

It will be noted (Table 10) that N and K had a highly significant influence on the yield of K, while lime surprisingly did not. The apparent lack of significant influence by lime is probably due to the fact that the lime had diametrically opposed effects on the yield of K on each soil. It is quite possible that these opposing effects tended to cancel each other in the overall analysis of variance as discussed later. Table 10 further reveals that there was a highly significant difference between soils with respect to yields of K. There were very marked N x soil and lime x soil interactions which were significant at the 1 per cent level.

In order to facilitate closer study of the factors affecting K uptake separate analyses of variance were conducted on the yield of K data for each soil. These results are reported in Table 11. It is apparent from the outset that there were significant differences between replicates on each soil. This again indicates that environmental conditions were not as uniform as was indicated by the low F value for Replicates in Table 10. As was indicated in Table 10, K application had a significant main effect on K uptake for both soils with the significance being at the 5 per cent level on the Maleb soil and at the 1 per cent level on the Cooking Lake soil. The most striking observation in Table 11, however, was the fact that lime, which had been indicated as an insignificant factor in Table 10, had a highly significant main effect with respect to K uptake on both soils. This lends support to the theory advanced earlier that significant lime effects, if diametrically opposed on each soil and of approximately the same magnitude,

TABLE 10. ANALYSIS OF VARIANCE FOR YIELD OF POTASSIUM ON
MALEB AND COOKING LAKE A HORIZONS

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F Value
Replicates	1	0.096	0.096	0.014
N	2	96.731	48.365	7.231**
K	2	92.060	46.030	6.882**
Lime	2	2.347	1.174	0.175
Soil	1	3,542.861	3,542.861	529.734**
N x K	4	37.842	9.460	1.414
N x Lime	4	44.585	11.146	1.666
K x Lime	4	15.918	3.980	0.595
N x Soil	2	174.133	87.066	13.018**
K x Soil	2	1.760	0.880	0.131
Lime x Soil	2	222.105	111.052	16.604**
N x K x Lime	8	36.284	4.536	0.678
N x K x Soil	4	36.518	9.130	1.365
N x Lime x Soil	4	10.809	2.702	0.404
K x Lime x Soil	4	17.082	4.270	0.638
N x K x Lime x Soil	8	45.432	5.679	0.849
Error	53	354.464	6.688	
Total	107	4,731.027		

** Denotes significance at the 1% level.

TABLE 11. ANALYSIS OF VARIANCE FOR YIELD OF K ON
THE INDIVIDUAL SOILS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
<u>Maleb A Horizon (Profile 1)</u>				
Replicates	1	39.938	39.938	6.070*
N	2	253.689	126.844	19.278**
K	2	46.980	23.490	3.570*
Lime	2	131.590	65.795	10.000**
N x K	4	43.346	10.836	1.647
N x Lime	4	45.758	11.440	1.739
K x Lime	4	25.330	6.332	0.962
N x K x Lime	8	47.199	5.900	0.897
Error	26	171.073	6.580	
Total	53	804.903		
<u>Cooking Lake A Horizon (Profile 1)</u>				
Replicates	1	45.650	45.650	12.122**
N	2	17.177	8.588	2.281
K	2	46.842	23.421	6.219**
Lime	2	92.865	46.432	12.330**
N x K	4	31.015	7.754	2.059
N x Lime	4	9.635	2.409	0.640
K x Lime	4	7.668	1.917	0.509
N x K x Lime	8	34.523	4.315	1.146
Error	26	97.910	3.766	
Total	53	383.286		

* Denotes significance at the 5% level.

** Denotes significance at the 1% level.

could tend to mask each other in a bulk analysis of variance as reported in Table 10. There were no significant nutrient interactions with respect to K uptake on the two soils.

(d) Calcium yields

Table 12 presents the yields of Ca on Maleb and Cooking Lake A horizons as a function of applied N, K, and lime. It will be noted that at the zero and 5 T./ac. level of lime the yield of Ca for the Maleb soil tended to be higher than the corresponding values on the Cooking Lake soil. At the 10 T./ac. level of lime, however, there was very little difference in the values between soils. At the various N-K combinations there seemed to be a weak trend towards increased yields of Ca on the Maleb and a strong trend on the Cooking Lake as the level of applied lime was increased. The exact effect of K on Ca uptake was difficult to determine in that it was neither consistent, nor was there a pronounced trend. On the Maleb soil, increased N rates tended to produce increased yields of Ca, the most marked increases being observed at the zero and 5 T./ac. levels of lime.

At first glance the data for Ca uptake on the Cooking Lake soil does not appear to depict any real trend as the level of N is increased. Since K had no significant effect on Ca uptake on the Cooking Lake soil (Table 14) it seems feasible that the yields of Ca corresponding to the three K rates at each value of N should be averaged. If this is done there now appears to be a consistent trend. At each level of lime there was an initial increase in yield of Ca and a subsequent decrease as the level of N was increased.

It will be observed (Table 13) that N and lime exerted a highly significant influence on the yield of Ca. The difference between soils was significant at the 1 per cent level as were the N x soil and lime x soil interactions.

TABLE 12. YIELDS OF CALCIUM (mg.) FOR NUTRIENT COMBINATIONS
APPLIED TO MALEB AND COOKING LAKE A HORIZONS
(Average of 2 Replications)

N (lb./ac.)	K (lb./ac.)	Lime (T./ac.)		
		0	5	10
<u>Maleb A Horizon (Profile 1)</u>				
0	0	4.87	4.84	4.72
0	150	4.44	4.75	4.76
0	300	4.51	6.04	4.92
150	0	5.34	5.87	5.39
150	150	5.79	6.04	5.54
150	300	5.90	6.01	6.58
300	0	5.44	6.81	5.67
300	150	7.78	6.56	5.76
300	300	7.70	6.84	6.61
<u>Cooking Lake A Horizon (Profile 1)</u>				
0	0	2.39	5.26	4.74
0	150	2.51	5.04	6.27
0	300	3.20	3.52	4.12
150	0	2.55	5.55	5.22
150	150	4.43	3.52	5.57
150	300	2.66	5.28	7.08
300	0	1.74	3.76	4.16
300	150	1.97	3.78	5.30
300	300	2.62	4.88	5.02

TABLE 13. ANALYSIS OF VARIANCE FOR YIELD OF CALCIUM ON
MALEB AND COOKING LAKE A HORIZONS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
Replicates	1	1.993	1.993	1.969
N	2	11.718	5.859	5.788**
K	2	4.654	2.327	2.299
Lime	2	30.358	15.179	14.996**
Soil	1	69.456	69.456	68.623**
N x K	4	4.135	1.034	1.021
N x Lime	4	1.722	0.430	0.425
K x Lime	4	4.813	1.203	1.188
N x Soil	2	22.738	11.369	11.232**
K x Soil	2	0.881	0.440	0.435
Lime x Soil	2	35.641	17.821	17.606**
N x K x Lime	8	7.744	0.968	0.956
N x K x Soil	4	2.700	0.675	0.666
N x Lime x Soil	4	2.061	0.515	0.508
K x Lime x Soil	4	2.089	0.522	0.516
N x K x Lime x Soil	8	11.888	1.486	1.468
Error	53	53.643	1.012	
Total	107	268.236		

** Denotes significance at the 1% level.

TABLE 14. ANALYSIS OF VARIANCE FOR YIELD OF CALCIUM
ON THE INDIVIDUAL SOILS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
<u>Maleb A Horizon (Profile 1)</u>				
Replicates	1	1.497	1.497	2.073
N	2	26.230	13.115	18.176**
K	2	4.229	2.114	2.930
Lime	2	1.614	0.807	1.119
N x K	4	1.380	0.345	0.478
N x Lime	4	2.796	0.699	0.969
K x Lime	4	1.424	0.356	0.493
N x K x Lime	8	5.550	0.694	0.961
Error	26	18.760	0.722	
Total	53	63.480		
<u>Cooking Lake A Horizon (Profile 1)</u>				
Replicates	1	10.367	10.367	10.776**
N	2	8.227	4.113	4.276*
K	2	1.307	0.653	0.679
Lime	2	64.385	32.192	33.464**
N x K	4	5.456	1.364	1.418
N x Lime	4	0.987	0.247	0.257
K x Lime	4	5.479	1.370	1.424
N x K x Lime	8	14.080	1.760	1.830
Error	26	25.012	0.962	
Total	53	135.300		

* Denotes significance at the 5% level.

** Denotes significance at the 1% level.

The analysis of variance for the yield of Ca data on the individual soils (Table 14) facilitates a closer study of the N and lime main effects. It will be noted that the highly significant main effect of N on Ca uptake reported in Table 13 is attributable to a large extent to the N effect on the Maleb soil. The N main effect was significant at the 1 per cent level on this soil but only at the 5 per cent level on the Cooking Lake soil. The significant lime effect reported in Table 13 was almost exclusively accounted for by the Cooking Lake soil. One other fact revealed by the individual analyses of variance was the existence of a highly significant difference between replicates on the Cooking Lake soil which again indicates a lack of uniformity in environmental conditions.

2. C Horizons for Maleb and Cooking Lake

(a) Dry matter yields

The yield response to N and K on the Maleb and Cooking Lake C horizons is summarized in Table 15 and portrayed graphically in Fig. 4 for easier scrutiny. Since K had no significant effect on the yield of dry matter the yield values at the three K levels were averaged and these averages were plotted against the rates of N. It can be seen from Fig. 4 that on each soil there was a net increase in yield of dry matter as the rate of N was increased. The overall yield of dry matter was significantly higher (1 per cent level, Table 16) on the Maleb soil than on the Cooking Lake. In each case the response pattern was curvilinear but on the Maleb soil yield increases between the 150 and 300 lb./ac. levels of N proceeded at a decreasing rate. On the Cooking Lake soil, however, the yield increases between the same two levels proceeded at an increasing rate as can be seen from the change in slope of the response curve. If the difference in yield between the zero and 300 lb./ac. N rates (Table 15) is used as the criterion

TABLE 15. YIELD RESPONSE (g.) TO NITROGEN AND POTASSIUM ON MALEB
AND COOKING LAKE C HORIZONS
(Average of 3 Replications)

N (lb./ac.)	K (lb./ac.)			
	0	150	300	Av.
<u>Maleb C Horizon (Profile 1)</u>				
0	0.82	0.73	0.63	0.73
150	0.80	0.78	0.88	0.82
300	0.94	0.84	0.84	0.87
<u>Cooking Lake C Horizon (Profile 1)</u>				
0	0.59	0.61	0.69	0.63
150	0.69	0.60	0.66	0.65
300	0.92	0.69	0.77	0.79

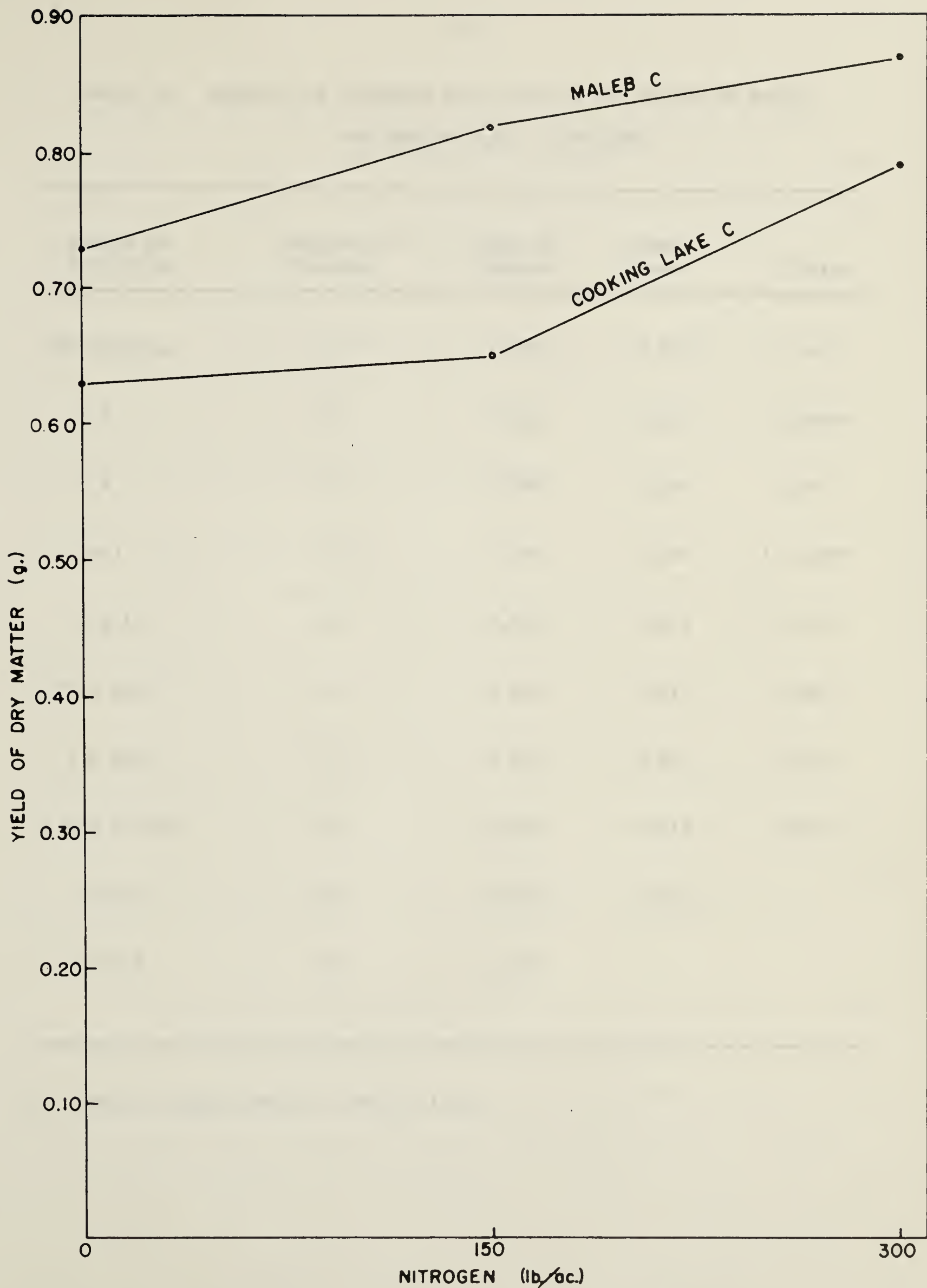


Figure 4. Yield of dry matter as a function of applied N on Maleb (Profile 1) and Cooking Lake (Profile 1) C horizons (Av. of 3 levels of K).

TABLE 16. ANALYSIS OF VARIANCE FOR YIELD OF DRY MATTER ON MALEB
AND COOKING LAKE C HORIZONS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
Replicates	2	0.078	0.939	2.346
N	2	0.227	0.114	6.856**
K	2	0.068	0.034	2.059
Soil	1	0.185	0.185	11.150**
N x K	4	0.050	0.012	0.750
N x Soil	2	0.023	0.012	0.694
K x Soil	2	0.012	0.006	0.364
N x K x Soil	4	0.070	0.018	1.060
Error	34	0.564	0.016	
Total	53	1.278		

** Denotes significance at the 1% level.

for assessing yield response on the two soils the results are intriguing. Despite the disparity in absolute yields it appears that the yield response to added N was slightly greater on the Cooking Lake soil than on the Maleb. This observation is further substantiated by the fact that N had no significant effect on yield on the Maleb soil (Table 17) but had a significant main effect on the Cooking Lake soil (5 per cent level, Table 17). In fact, the significant N effect reported in Table 16 appears to be almost entirely attributable to the Cooking Lake soil. There were no significant nutrient interactions operative on these soils.

(b) Nitrogen yields

Yields of N were also different on the Maleb and Cooking Lake C horizons (Table 18, Fig. 5). It will be noted from Fig. 5 that the N response pattern was very similar on both soils between the zero and 150 lb./ac. rates of N. This is apparent from the similarity of the slopes. Beyond the 150 lb./ac. N level, however, the N response patterns of the two soils are quite different. Although there was an increase in N uptake in both cases, the rate of uptake on the Maleb soil proceeded at a decreasing rate while the rate of uptake on the Cooking Lake soil showed a marked increase.

If Table 18 is now compared with Table 6 it is possible to obtain a measure of the N response on the C horizons of the two soils as compared to the N response on the A horizons. It will be recalled from Fig. 2 and 3 that increased rates of applied lime had a depressive effect on N uptake on the Maleb A horizon. On the Cooking Lake A horizon, however, lime tended to increase N uptake. Since no lime was added to the C horizons of these soils, the data in Table 18 facilitate in addition an assessment of the effect of native lime as opposed to applied lime with respect to N uptake.

TABLE 17. ANALYSIS OF VARIANCE FOR YIELD OF DRY MATTER ON
THE INDIVIDUAL SOILS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
<u>Maleb C Horizon (Profile 1)</u>				
Replicates	2	0.081	0.041	2.160
N	2	0.086	0.043	2.240
K	2	0.039	0.019	1.016
N x K	4	0.070	0.017	0.913
Error	16	0.306	0.019	
Total	26	0.583		
<u>Cooking Lake C Horizon (Profile 1)</u>				
Replicates	2	0.034	0.017	1.215
N	2	0.149	0.074	5.106*
K	2	0.051	0.026	1.763
N x K	4	0.060	0.015	1.034
Error	16	0.234	0.014	
Total	26	0.530		

* Denotes significance at the 5% level.

TABLE 18. YIELD OF NITROGEN (mg.) ON MALEB AND COOKING LAKE C
HORIZONS AS A FUNCTION OF APPLIED
NITROGEN AND POTASSIUM
(Average of 3 Replications)

N (lb./ac.)	K (lb./ac.)			
	0	150	300	Av.
<u>Maleb C Horizon (Profile 1)</u>				
0	10.85	9.44	9.87	10.05
150	12.34	12.14	13.49	12.66
300	16.45	13.98	13.88	14.77
<u>Cooking Lake C Horizon (Profile 1)</u>				
0	8.80	8.64	9.34	8.93
150	12.11	10.71	11.45	11.42
300	18.34	14.86	14.06	15.75

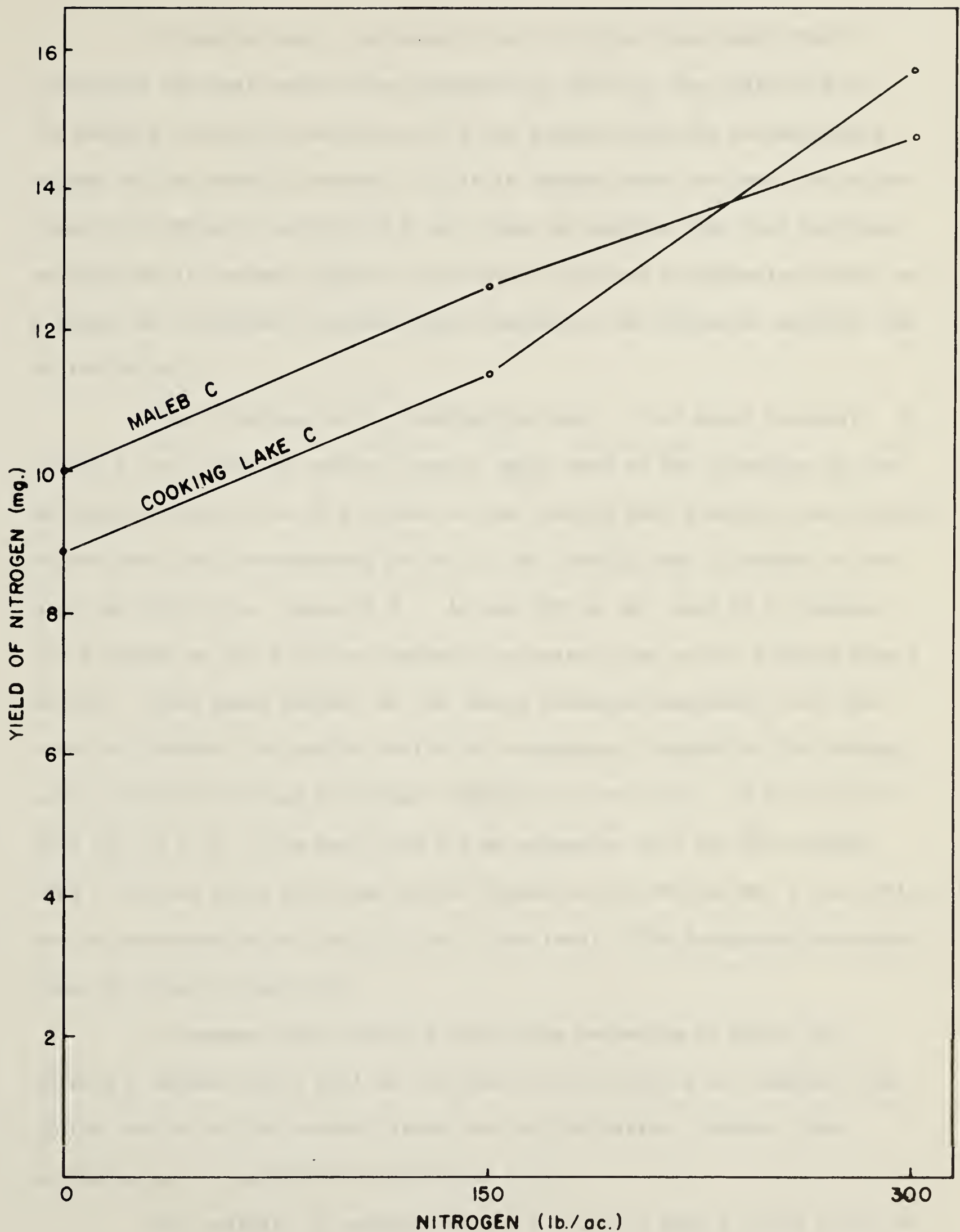


Figure 5. Yield of N on Maleb (Profile 1) and Cooking Lake (Profile 1) C horizons as a function of applied N (Av. of 3 K levels).

It can be seen, that even at the 10 T./ac. lime level which represents the most severe lime treatment in Table 6, the yield of N on the Maleb A horizon at each rate of N was greater than the corresponding values for the Maleb C horizon. If it is assumed that the level of native lime in the Maleb C and the 10 T./ac. level of applied lime both provided excess lime it becomes apparent that native lime had a depressive effect on N uptake on the Maleb C horizon quite similar to the effect of applied lime on the Maleb A.

The situation on the Cooking Lake soil is of equal interest. If the 10 T./ac. level of applied lime is again used as the criterion it can be seen that the yield of N values on the Cooking Lake A horizon are slightly higher than the corresponding values on the Cooking Lake C horizon at the zero and 150 lb./ac. rates of N. At the 300 lb./ac. rate of N, however, the N uptake on the C horizon markedly surpassed that on the Cooking Lake A horizon. This lends support to the theory advanced previously that lime seems to increase dry matter yields and encourages N uptake on the Cooking Lake soil by correcting a nutrient imbalance in the soil. It may well be that the 10 T./ac. lime level was not an excessive rate for the Cooking Lake A horizon since the slope of the ligand at the 300 lb./ac. N rate (Fig. 3) was an ascending one at the 10 T./ac. lime level. The foregoing discussion seems to support this view.

It appears then that the underlying mechanism by which lime affects N uptake from a soil is the same for both native and applied lime. If the results of the present study are any indication, however, this mechanism may be different on different soils.

The analysis of variance of the yield of N data for the soils was done in two ways, namely (1) a bulk analysis incorporating the data for

both soils, and (2) individual analyses of variance treating each soil as a separate entity. These results are presented in Tables 19 and 20. It will be noted from Table 19 that the only variable which had a significant effect on the yield of N was the level of applied N. The individual analyses of variance reported in Table 20 substantiate this fact and further indicate that the N main effect was highly significant on both soils but was somewhat more pronounced on the Cooking Lake soil.

(c) Potassium yields

Yields of K at the three K levels were averaged (Table 21), since applied K proved to be an insignificant factor with respect to K uptake (Tables 22 and 23). The averages were plotted against the rates of N as shown in Fig. 6. The resulting curves present a general picture of how K uptake varies with applied N on the two soils. As can be seen, the K response pattern on each soil was curvilinear. Whereas on the Cooking Lake soil the response curve was an ascending one with an increasing slope beyond the 150 lb./ac. N rate, the curve on the Maleb soil had a diminished slope beyond the aforementioned N rate and appeared, as it were, to be flattening out towards some equilibrium level.

The difference in yield of K between the two soils shown in Fig. 6 was significant at the 1 per cent level (Table 22). Nitrogen had a highly significant main effect on K uptake, but none of the other main effects or interactions was significant. The analysis of variance of the individual soils (Table 23) substantiates these findings and indicates that the major N effect was on the Cooking Lake soil. The N main effect on the Maleb soil was just below the value required for significance at the 5 per cent level.

It is apparent from these data that the level of native K in the two soils had a stronger bearing on K uptake than did the applied K.

TABLE 19. ANALYSIS OF VARIANCE FOR YIELD OF NITROGEN ON MALEB
AND COOKING LAKE C HORIZONS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
Replicates	2	1.615	0.807	0.123
N	2	301.476	150.738	22.896**
K	2	23.797	11.898	1.807
Soil	1	2.411	2.411	0.366
N x K	4	24.736	6.184	0.939
N x Soil	2	13.343	6.671	1.013
K x Soil	2	1.047	0.524	0.079
N x K x Soil	4	5.590	1.398	0.212
Error	34	223.837	6.583	
Total	53	597.853		

** Denotes significance at the 1% level.

TABLE 20. ANALYSIS OF VARIANCE FOR YIELD OF N ON THE TWO SOILS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
<u>Maleb C Horizon (Profile 1)</u>				
Replicates	2	14.232	7.116	1.165
N	2	100.174	50.087	8.192**
K	2	9.737	4.868	0.796
N x K	4	10.505	2.626	0.430
Error	16	97.825	6.114	
Total	26	232.474		
<u>Cooking Lake C Horizon (Profile 1)</u>				
Replicates	2	10.797	5.399	0.842
N	2	214.645	107.322	16.737**
K	2	15.108	7.554	1.178
N x K	4	19.823	4.956	0.773
Error	16	102.595	6.402	
Total	26	362.967		

** Denotes significance at the 1% level.

TABLE 21. YIELD OF POTASSIUM (mg.) ON MALEB AND COOKING LAKE C
HORIZONS AS A FUNCTION OF APPLIED
NITROGEN AND POTASSIUM

(Average of 3 Replications)

N (lb./ac.)	K (lb./ac.)			Av.
	0	150	300	
<u>Maleb C Horizon (Profile 1)</u>				
0	10.40	10.62	9.55	10.19
150	11.92	12.16	15.15	13.08
300	13.92	12.46	15.07	13.82
<u>Cooking Lake C Horizon (Profile 1)</u>				
0	7.12	6.90	8.33	7.45
150	9.13	8.06	8.60	8.60
300	9.88	9.39	13.52	10.93

TABLE 22. ANALYSIS OF VARIANCE FOR YIELD OF POTASSIUM ON MALEB
AND COOKING LAKE C HORIZONS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
Replicates	2	26.609	13.304	1.846
N	2	84.496	42.248	5.862**
K	2	14.320	7.160	0.993
Soil	1	121.710	121.710	16.889**
N x K	4	5.644	1.411	0.195
N x Soil	2	16.755	8.378	1.162
K x Soil	2	6.375	3.188	0.442
N x K x Soil	4	36.585	9.146	1.269
Error	34	245.014	7.206	
Total	53	557.508		

** Denotes significance at the 1% level.

TABLE 23. ANALYSIS OF VARIANCE FOR YIELD OF K ON THE INDIVIDUAL SOILS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
<u>Maleb C Horizon (Profile 1)</u>				
Replicates	2	33.814	16.907	1.995
N	2	44.634	22.317	2.636
K	2	0.940	0.470	0.056
N x K	4	26.00	6.525	0.771
Error	16	135.461	8.466	
Total	26	240.949		
<u>Cooking Lake C Horizon (Profile 1)</u>				
Replicates	2	13.234	6.617	1.190
N	2	56.617	28.308	5.083*
K	2	19.755	9.878	1.774
N x K	4	16.130	4.032	0.724
Error	16	89.112	5.569	
Total	26	194.848		

* Denotes significance at the 5% level.

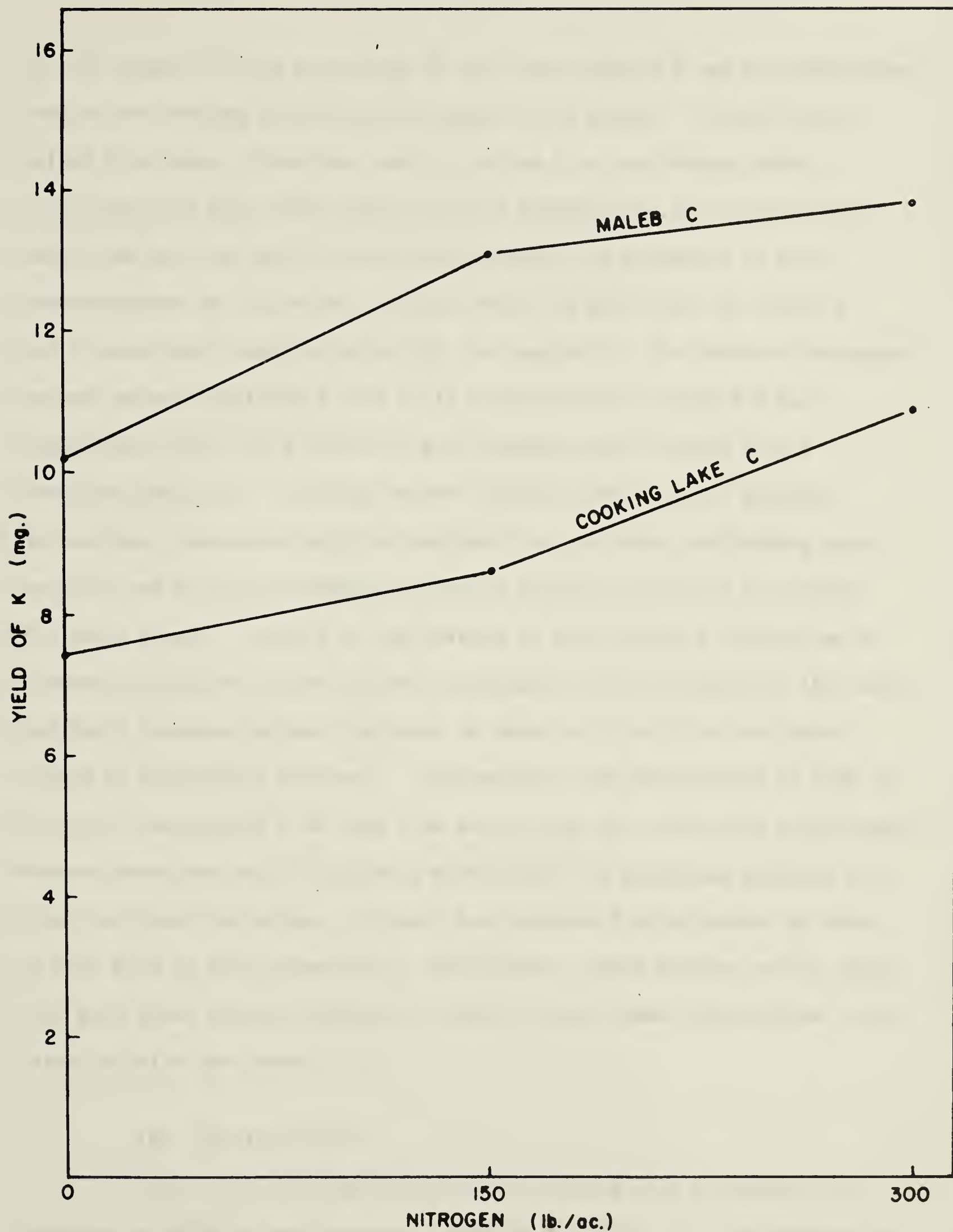


Figure 6. Yield of K on Maleb (Profile 1) and Cooking Lake (Profile 1) C horizons as a function of applied N (Av. of 3 K levels).

Figure 6. Yield of R on Maleb (Profile I) and Cooking Lake (Profile I) C horizons as a function of applied N (Av. of 3 K levels).



In this regard, it was surprising to note that applied K was not significant even on the Cooking Lake soil with respect to K uptake. It will be recalled from Table 2 that the level of native K in the Cooking Lake C horizon was not only lower than the Maleb analogue but also considerably lower than the two upper levels of applied K. The situation is more understandable on the Maleb C horizon where the high level of native K could conceivably mask the effect of the applied K. The observed phenomenon assumes added significance when it is considered that applied K had a significant effect on K uptake on both the Maleb and Cooking Lake A horizons (Table 11). It would appear then that some factor, possibly native lime, interfered with the applied K in the Maleb and Cooking Lake C horizons and forced the indicator crop to utilize the native K reservoir for its K supply. In view of the absence of more detailed information no further explanation of the observed phenomenon will be offered at this point and the K response on the C horizons of these soils will be considered simply as behavioural patterns. Nevertheless, this observation of lack of K uptake from applied K on high lime soils could have important significance because there are soils in Alberta with fairly low potassium contents and free lime near the surface. Walker¹ has observed K deficiencies on soils of this kind in the Lacombe area. Furthermore, these results are in agreement with other workers (Woodruff, 1955) who have found that high Ca levels interfere with the uptake of K.

(d) Calcium yields

The yields of Ca on the Maleb and Cooking Lake C horizons are reported in Table 24 and portrayed graphically in Fig. 7. The analysis of

¹ Mr. D. Walker, Lacombe Experimental Farm. Personal correspondence.

TABLE 24. YIELD OF CALCIUM (mg.) ON MALEB AND COOKING LAKE C
HORIZONS AS A FUNCTION OF APPLIED
NITROGEN AND POTASSIUM

(Average of 3 Replications)

N (lb./ac.)	K (lb./ac.)			
	0	150	300	Av.
<u>Maleb C Horizon (Profile 1)</u>				
0	3.99	4.13	3.73	3.95
150	4.32	3.84	4.96	4.37
300	4.82	4.67	4.28	4.59
<u>Cooking Lake C Horizon (Profile 1)</u>				
0	3.71	3.91	4.85	4.16
150	4.30	3.99	4.38	4.22
300	6.29	4.81	5.17	5.42

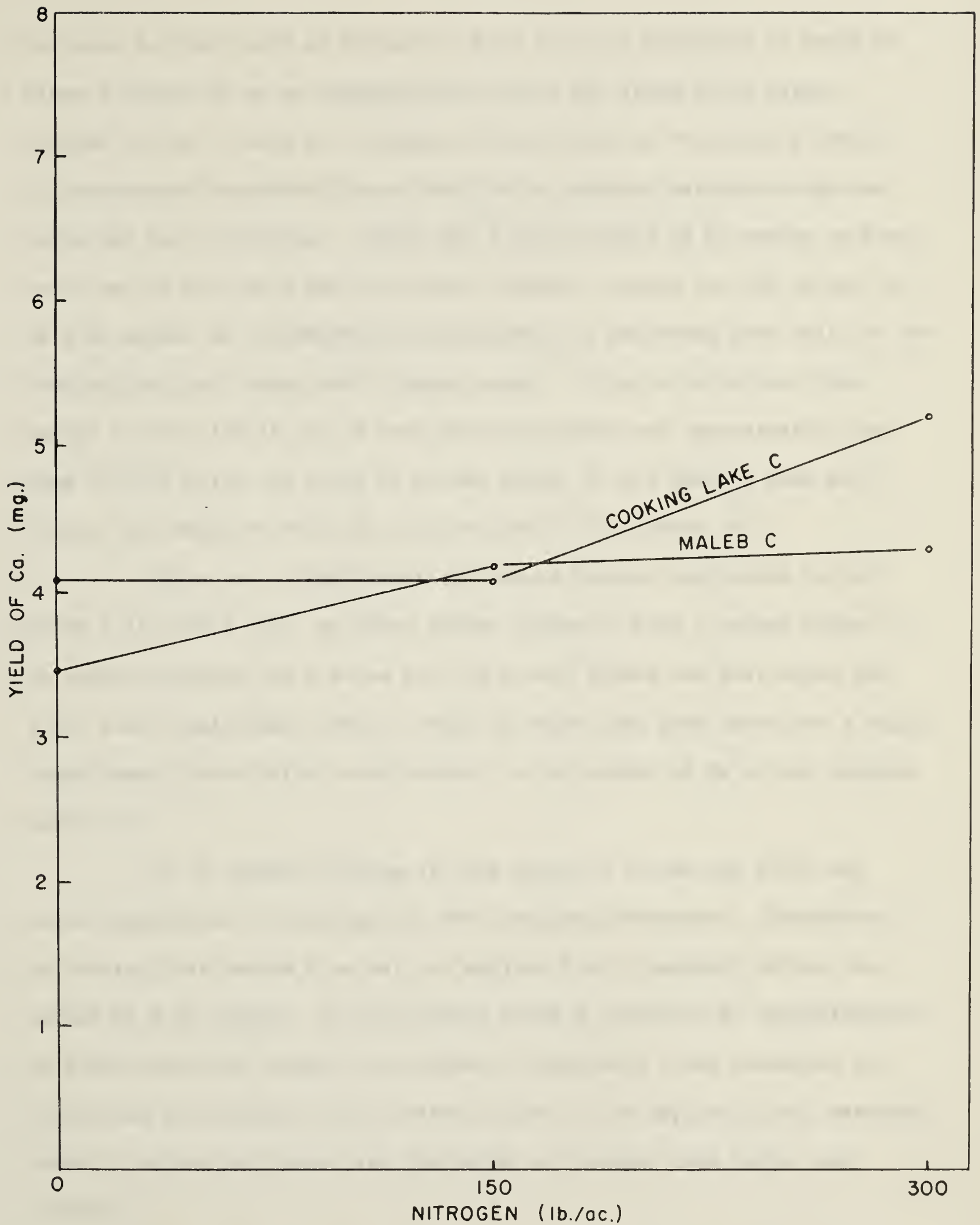


Figure 7. Yield of calcium on Maleb (Profile 1) and Cooking Lake (Profile 1) C horizons as a function of applied N (Av. of 3 K levels).

variance for the yield of Ca data of both soils is presented in Table 25. Since K proved to be an insignificant factor the yield of Ca values plotted in Fig. 7 were the averages of the values at the three K levels. It can be seen from this Figure that the Ca response pattern on the two soils was quite different. There was a net increase in Ca uptake on both soils as the rate of N was increased. However, beyond the 150 lb./ac. N rate Ca uptake on the Maleb soil proceeded at a decreased rate while on the Cooking Lake soil there was a sudden surge. It can also be seen that except for the 150 lb./ac. N rate where Ca uptake was approximately the same on both soils the yield of Ca was higher on the Cooking Lake soil than on the Maleb at both the zero and 300 lb./ac. rates of N.

There was a significant difference between replicates on the Maleb soil (Table 26). No other factor seemed to have a marked effect on Ca uptake although the F value for the N main effect was just below the 5 per cent significance level. Table 26 shows also that there was a highly significant N main effect with respect to the uptake of Ca on the Cooking Lake soil.

It is perhaps fitting at this point to review the first and second hypotheses in the light of the foregoing discussion. Hypothesis 1 had stated that native K as well as applied K will markedly affect the uptake of N by plants. In the present study K proved to be insignificant on both soils with respect to N uptake. Hypothesis 1 was therefore rejected and the converse, that neither native K nor applied K will markedly affect N uptake by plants from the Maleb and Cooking Lake soils, was accepted.

Hypothesis 2 stated that native lime and added lime will directly or indirectly reduce N uptake by plants. This hypothesis was accepted

TABLE 25. ANALYSIS OF VARIANCE FOR YIELD OF CALCIUM ON MALEB
AND COOKING LAKE C HORIZONS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
Replicates	2	1.153	0.577	1.034
N	2	8.848	4.424	7.931**
K	2	1.402	0.701	1.256
Soil	1	1.194	1.194	2.140
N x K	4	3.606	0.902	1.616
N x Soil	2	2.251	1.126	2.017
K x Soil	2	0.524	0.262	0.469
N x K x Soil	4	3.091	0.773	1.385
Error	34	18.964	0.558	
Total	53	41.033		

** Denotes significance at the 1% level.

TABLE 26. ANALYSIS OF VARIANCE FOR YIELD OF CALCIUM ON THE
INDIVIDUAL SOILS

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F Value
<u>Maleb C Horizon (Profile 1)</u>				
Replicates	2	2.338	1.169	3.747*
N	2	1.910	0.955	3.053
K	2	0.124	0.062	0.199
N x K	4	2.458	0.614	1.964
Error	16	5.005	0.312	
Total	26	11.835		
<u>Cooking Lake C Horizon (Profile 1)</u>				
Replicates	2	2.990	1.495	2.447
N	2	9.188	4.594	7.513**
K	2	1.801	0.901	1.473
N x K	4	4.240	1.060	1.733
Error	16	9.784	0.611	
Total	26	28.004		

* Denotes significance at the 5% level.

** Denotes significance at the 1% level.

with some modification. It will be recalled (Tables 6 and 18) that lime reduced N uptake on the Maleb soil but augmented N uptake to some extent on the Cooking Lake soil through what was believed to be a correction of a nutrient imbalance. Hypothesis 2 was therefore modified as follows: native lime and added lime will directly or indirectly reduce N uptake by plants on some soils. Where a nutrient imbalance exists, however, lime can augment N uptake by correcting the nutrient imbalance.

2. SOIL FRACTIONATION STUDIES

The main purpose of using N^{15} in this phase of the investigation was to label a definite fraction of soil nitrogen by the introduction of a known amount of tagged nitrogen. This tagged form will equilibrate with native soil nitrogen. The mixture of native and tagged nitrogen, when submitted to chemical and biological processes may be transformed to other forms or fractions of soil nitrogen.

The soil N fraction labelled in this study was the inorganic NH_4^+ fraction which is extractable by 1 N KCl and the N^{15} was added as $N^{15}H_4NO_3$. Two fundamental assumptions were made at the outset of the experiment. Firstly, it was assumed that the added tagged N would become fully equilibrated with the native soil N. The second was that isotope effects would be small in magnitude, and that the N^{15} atoms would be transformed in a similar manner to the N^{14} atoms. Some isotope effects might exist because N^{14} bonds are more energetic and more easily broken than N^{15} bonds (Hoering, 1955). These are being neglected, however, since the maximum expected effect would be of the order of 4 per cent (Urey, 1947). In addition, it is almost impossible to evaluate such effects at the present time since the underlying processes are not known.

The Kjeldahl analyses for total organic and ammoniacal N were repeated until three determinations with a standard deviation of not greater than 2 per cent were obtained. These determinations were then averaged and the averages were used for subsequent calculations. The N^{15} determinations, however, were very tedious and time-consuming and consequently all reasonable measures to limit their number had to be employed. Initially duplicate determinations were made. When it became apparent that the concordance between duplicates was high, only one sample of each set of three Kjeldahl distillates was generally subjected to mass spectrometric analysis. The data for total organic and ammoniacal N and tagged N content of both soils after various incubation periods are presented in Table 27. The N^{15} values were expressed as excess atom per cent over the N^{15} content of normal soil N (0.38 atom per cent) as reported by Nier (1946), Rittenberg (1946), and Rankama (1954). The excess N^{15} atom percentage of the inorganic N pool of each soil after labelling at zero time was calculated from the following equation proposed by Jansson (1958):

$$C = \frac{n_2 c_2}{n_1 + n_2}$$

where C = excess atom per cent in the mixture

n_1 = me. N/100 g. (unlabelled soil)

n_2 = me. N/100 g. (labelled additive)

c_2 = excess N^{15} atom per cent of labelled additive.

The accuracy of the spectrometer measurements was very satisfactory and the standard deviation of replicate determinations on each sample was in general less than 1 per cent (Appendix 5 and 6). Appropriate corrections for air contamination were made where necessary but samples containing more than

TABLE 27. TOTAL N (me./100 g.) AND ATOM PER CENT EXCESS N¹⁵ IN DIFFERENT
SOIL N FRACTIONS AFTER VARIOUS INCUBATION PERIODS

Days	KCl Fraction		Distillable Acid-Soluble		Nondistillable Acid-Soluble		Acid-Insoluble Residue	
	Atom % N	Total N	Atom % N	Total N	Atom % N	Total N	Atom % N	Total N
Maleb A (Profile 2)								
0	58.70	4.59*	--	5.39	--	10.80	--	6.13
10	40.75	1.86	2.59	5.99	1.04	11.56	0.16	6.43
20	38.39	1.62	3.05	6.04	0.70	12.84	0.53	6.35
40	36.50	1.78	2.80	7.26	0.73	9.62	0.90	6.34
80	37.36	1.82	2.21	8.97	0.83	8.45	0.98	6.81
Cooking Lake A (Profile 1)								
0	61.00	4.44*	--	2.29	--	2.52	--	1.93
10	39.63	1.52	7.11	2.11	2.90	2.76	0.65	2.52
20	40.65	1.48	11.97	2.21	3.00	2.67	1.54	2.58
40	42.00	1.51	13.12	2.62	1.81	2.77	1.65	2.59
80	36.39	1.73	13.92	2.30	1.75	2.86	2.16	2.69

* Includes ammoniacal N initially in the KCl fraction as well as total N added.

3 per cent air were discarded in accordance with the recommendation of Rittenberg (1946).

It will be observed (Table 27) that in general the N^{15} percentages and the values for total N follow a similar pattern in the different fractions of each soil. In the inorganic KCl extracts, for example, both show an initial decrease in the early stages of incubation followed in most cases by a slight increase after about 20 days of incubation. This pattern is similar for both soils. In the distillable acid-soluble fraction as well as the acid-insoluble residue the general trend was one of a gradual increase with incubation time. Again the overall picture was similar on both soils, differing mainly in extent. The nondistillable acid-soluble fraction of both soils showed fluctuations in both per cent N^{15} and total N which were essentially the reverse of those observed in the inorganic fraction extracted by KCl. As the time of incubation increased there was an initial increase in both total N and per cent N^{15} and then a subsequent decrease with time in this nondistillable acid-soluble fraction. This observation is in line with the findings of Stewart et al. (1963) that there is an inverse relationship between the changes in inorganic N and those of the nondistillable acid-soluble N.

The excess values, however, merely provide a qualitative measure of the N transformations which occurred. In order to follow the transformations quantitatively the product of the excess values and the total N values was computed as per Jansson (1958) and the results are reported in Table 28. It should be stressed that no attempt was made to compile a nitrogen balance sheet per se. Rather, the objective here was to trace the movement and transformation of added inorganic N following equilibration with some of the major organic N fractions. It will be recalled from the flow

TABLE 28. DISTRIBUTION OF N¹⁵ (me./100 g.) IN DIFFERENT FRACTIONS OF
SOIL N AFTER VARIOUS PERIODS OF INCUBATION

Days	KCl Extract	Distillable Acid-Soluble	Nondistillable Acid-Soluble	Acid-Insoluble Residue
Maleb A (Profile 2)				
0	1.33	--	--	--
10	0.76	0.16	0.12	0.01
20	0.62	0.18	0.09	0.03
40	0.65	0.20	0.07	0.06
80	0.68	0.20	0.07	0.07
Cooking Lake A (Profile 1)				
0	1.33	--	--	--
10	0.60	0.15	0.08	0.02
20	0.60	0.26	0.08	0.04
40	0.63	0.34	0.05	0.04
80	0.63	0.32	0.05	0.06

chart of soil fractionation presented previously that the composition of the various fractions was as follows:

KCl extract $\longrightarrow$ Exchangeable NH_4^+ + Soluble NO_3^-

Distillable acid-soluble fraction $\longrightarrow$ Hydrolyzed NH_4^+ and Amino sugars

Nondistillable acid-soluble fraction $\longrightarrow$ Amino acids and acid-soluble humin

Acid-insoluble residue $\longrightarrow$ Fixed NH_4^+ and insoluble humin

It can be seen from Table 28 that a substantial portion of the added N^{15} in both soils remained in inorganic form. This is more apparent from Table 29 where the N^{15} content of each soil N fraction is expressed as a percentage of the amount of N^{15} initially added. Over 40 per cent of the added N^{15} in both soils remained in inorganic form throughout the incubation period. This is due in part to the relatively large amount of N^{15} initially added and agrees with the findings of Stewart et al. (1963). In contrast to these workers, however, significant amounts of tagged N were detected in the distillable acid-soluble fraction of both soils. There was also a trend towards increased transformation of the added N to the fixed NH_4^+ and insoluble humin forms in the acid-insoluble residue as incubation time increased. The distillable acid-soluble fraction and the acid-insoluble residue are not believed to contribute significantly to the inorganic N pool, and added N after immobilization in these fractions is not subject to ready mineralization. In this connection it was interesting to note that the Cooking Lake soil, despite its lower total N content, immobilized more of the added N in these aforementioned fractions combined than did the Maleb soil. Comparison of the distillable acid-soluble fraction of the two soils illustrates this observation even more clearly. Both in absolute amounts (Table 28) and percentages of the labelled additive (Table 29) the

TABLE 29. PERCENTAGES OF ADDED N¹⁵ FOUND IN DIFFERENT FRACTIONS OF
SOIL N AFTER VARIOUS INCUBATION PERIODS

Days	KCl Extract	Distillable Acid-Soluble	Nondistillable Acid-Soluble	Acid-Insoluble Residue
<u>Maleb A (Profile 2)</u>				
0	100	--	--	--
10	57.14	12.03	9.02	0.75
20	46.61	13.53	6.77	2.25
40	48.87	15.04	5.26	4.50
80	51.12	15.04	5.26	5.26
<u>Cooking Lake A (Profile 1)</u>				
0	100	--	--	--
10	45.11	11.28	6.01	1.50
20	45.11	19.55	6.01	3.00
40	47.36	25.56	3.76	3.00
80	47.36	24.06	3.76	4.50

immobilization process in the Cooking Lake soil was more noticeable. This helps to explain why the dry matter yield and N uptake by barley were so poor on the Cooking Lake soil as compared to the Maleb. The underlying mechanism is not known but it is apparent that some factor inherent in the Cooking Lake soil promoted rapid immobilization of the added N thus reducing the amount available for plant usage. Perhaps clay mineral identification or organic matter characterization would help to elucidate the basic mechanism.

The nondistillable acid-soluble fractions of the two soils also provide an interesting comparison and help to explain the differences in N response observed earlier in the greenhouse studies. The exact significance of the absolute values is uncertain but there was a definite trend in the fluctuation of the N^{15} content with incubation time. Moreover, there seemed to be a definite relationship between changes in this fraction and changes in the inorganic N fraction. For visual scrutiny these variations in the two fractions are presented graphically as a function of incubation time in Fig. 8 and 9.

It can be seen from Fig. 8 that up to 20 days there was a decrease in the NH_4^+ fraction as the added N became transformed and some of this was immobilized in the various organic N fractions. Most of the immobilized N left the inorganic NH_4^+ fraction in the initial 10 days of incubation. Beyond the 20-day time span there was a slight increase in NH_4^+ -N as the pool became replenished with mineralized N from organic sources, and possibly reconversion of some nitrates to NH_4^+ .

The situation in Fig. 9 is the reverse of that observed in Fig. 8. It will be noted that the pattern in both cases is similar for the two soils, the main difference being one of extent. During the first 10 days of incubation there was a marked increase in N^{15} content (Fig. 9) of the

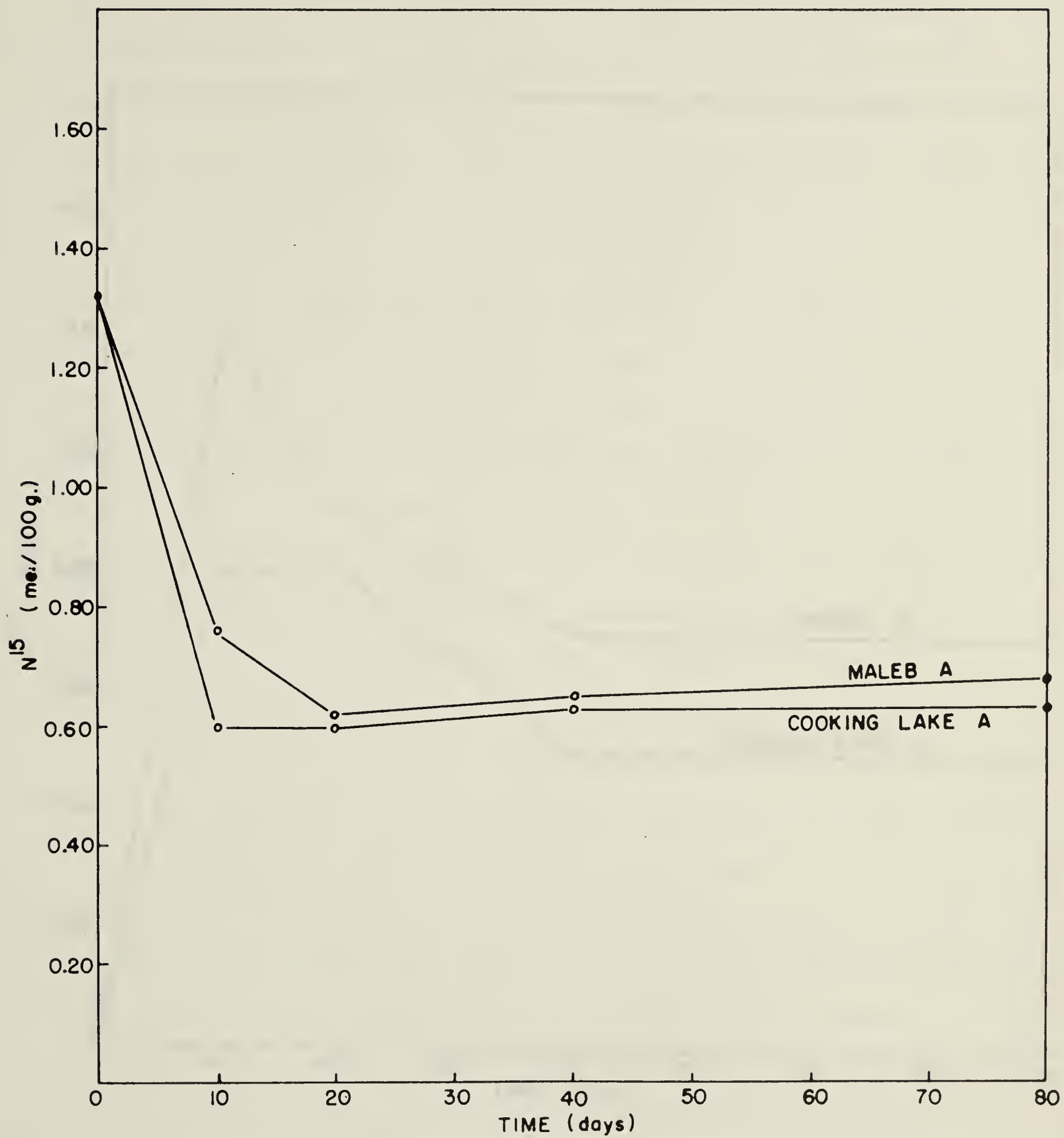


Figure 8. Fluctuations of added N^{15} in the KCl fraction of Maleb A (Profile 2) and Cooking Lake A (Profile 1) horizons with time.

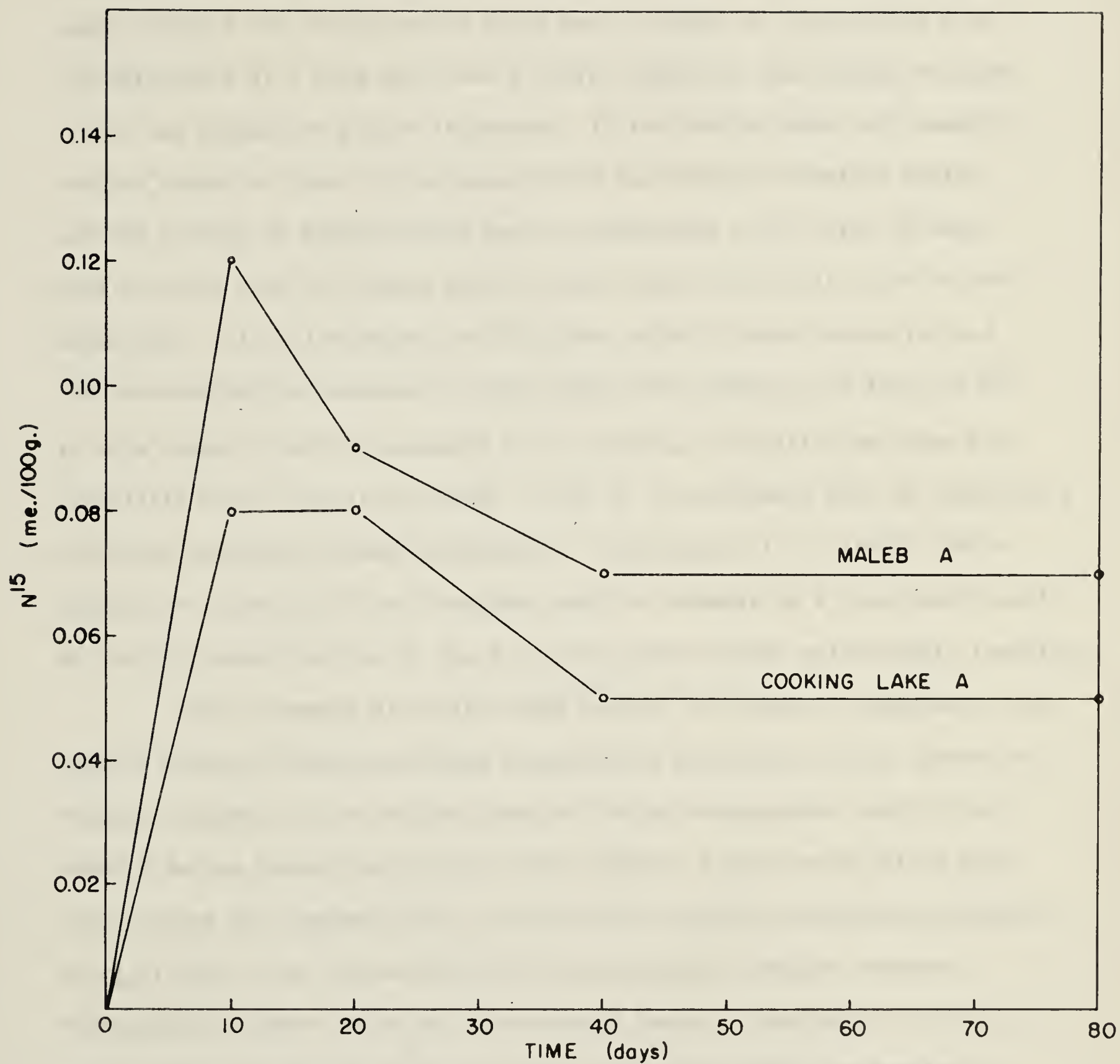


Figure 9. Fluctuations in N^{15} content of the nondistillable acid-soluble fractions of Maleb A (Profile 2) and Cooking Lake A (Profile 1) horizons with time.

nondistillable acid-soluble fractions of both soils. This is undoubtedly a result of the added N being transformed to amino acids and acid-soluble humin. Beyond the 10-day period there was a release of mineralized N in the Maleb soil at a rate which was at first rapid but then tended to taper off as the incubation period increased. In the Cooking Lake soil immobilization tended to level off between the 10 and 20-day incubation periods and the release of mineralized N was not detectable until after 20 days. Even then the rate of release did not quite match the initial rate in the Maleb soil. It will be noted too that even after 80 days incubation and with mineralization processes in both soils quite active, the level of N^{15} in this organic fraction appeared to be reaching an equilibrium value substantially above that at zero time. This is in accordance with Le Chatelier's principle regarding dynamic equilibria. Furthermore, it is likely that a removal of a portion of the inorganic pool for example by a crop would result in further mineralization of the N in the nondistillable acid-soluble fraction.

The foregoing discussion adds support to Jansson's hypothesis that added N does not become uniformly diluted with the total soil N. There is definite evidence of an "active fraction" which incorporates some of the added N during immobilization but later releases a portion of this N thus replenishing the inorganic pool. This active fraction was shown by Stewart et al. (1963) to be the nondistillable acid-soluble fraction composed essentially of amino acids and acid-soluble humin. From Table 27 it is apparent that the absolute size of this "active fraction" was greater in the Maleb soil than in the Cooking Lake. Fig. 9 shows in addition that more immobilized N entered the active fraction of the Maleb soil and a greater portion was subsequently released by mineralization than in the Cooking Lake soil. Furthermore, the rates of immobilization and subsequent release of

N by this fraction were more marked in the Maleb soil. These findings help to substantiate the theory advanced earlier, that the discrepancies in dry matter yield and N uptake between the A horizons of the two soils were due to a great extent to poorer N utilization by crops on the Cooking Lake soil. The Maleb A horizon used in the soil fractionation studies was taken from a different profile from that used in the greenhouse experiments. The chemical composition and physical characteristics of the two samples were essentially similar, however, as can be seen from Table 2. It was therefore reasoned that both soils would behave in a similar fashion.

In the light of these observations discussed previously, there appears to be sufficient justification for the acceptance of the third hypothesis. That is, for the soils under study, fluctuations in the magnitude of the "active fraction" of soil N were reflected in the relative amounts of N taken up by the Gateway barley from each soil.

3. NH_4^+ RETENTION STUDIES

The objective of this phase of the study was to further elucidate the differences in yield response and N uptake obtained in the greenhouse on the two soils. Specifically, an attempt was made to ascertain whether the main cause of the differences was the biochemical relationship discussed in the previous section or simply NH_4^+ retention properties peculiar to the individual soils. Since NH_4^+ retention in soils is generally attributed to the clay fraction, the extent of this retention is a reflection of the behaviour of the clay mineral suite.

It will be noted (Table 30) that the values for 1/3 atmosphere per cent were similar for all the soil horizons with the exception of

TABLE 30. AVERAGE WEIGHT OF SOIL IN DUPLICATE COLUMNS,
1/3 ATMOSPHERE PER CENT, AND MOISTURE
CONTENT AT TIME OF PACKING

Soil Horizon	Profile Designation	Soil Wt. (g.) (air-dried)	% H ₂ O	1/3 Atm. %
Maleb A	2	421.31	11.73	23.46
Maleb B	2	371.69	11.36	22.72
Maleb C	2	408.76	11.10	22.20
Cooking Lake A	1	433.92	8.31	16.62
Cooking Lake B	1	410.10	10.36	20.71
Cooking Lake C	1	434.21	10.36	20.72

Cooking Lake A. The moisture content of the samples was adjusted to a value approximately 1/2 the 1/3 atmosphere per cent just prior to packing. This was similar to the procedure followed by Chao et al. (1960) who used soil at a moisture content of 1/2 the moisture equivalent in their column study of $\text{SO}_4^{=}$ adsorption. The reason in both cases was to facilitate uniform packing.

The term "total N" in Table 31 refers to total ammoniacal and organic N. No modification was made to include nitrates since this was primarily an investigation of the strength with which soil in each horizon retained the NH_4^{+} ion. The inclusion of the B horizons in the study was done for the sake of completion, although only the A and C horizons of the two soils were used in the greenhouse investigations. One thing apparent from Table 31 is the fact that the N content of the segments in the Maleb columns was generally higher than those of the Cooking Lake. In most cases the values were twice as high, but in some cases they were as high as three times. It will be noted too that the top three segments of all the columns generally had higher N contents than the lower segments. It was mentioned earlier that leaching of the columns was continued until approximately 130 ml. of leachate had been collected. The sole exception to this procedure was the Cooking Lake B horizon in which an impermeable layer developed after the collection of approximately 60 ml. of leachate. In view of this difference in treatment a direct comparison of N content and N^{15} distribution in the two B horizons is perhaps not too meaningful. One other point of interest to the author was the fact that the N content of all leachates was the same with the exception of the leachate from the Maleb A which was much higher in N content than the others.

TABLE 31. TOTAL N (me./100 g.) OF EACH SOIL SEGMENT FOLLOWING
ADDITION OF 20 mg. N¹⁵ AND LEACHING
(Average of 2 Columns)

Soil Segments (inches)	A Horizon	B Horizon	C Horizon
<u>Maleb (Profile 2)</u>			
0 - 1	26.49	17.58	7.14
1 - 2	24.11	15.80	7.12
2 - 3	23.23	14.58	5.81
3 - 4	22.54	13.71	5.52
4 - 5	22.74	13.70	5.13
5 - 6	22.11	13.15	5.68
6 - 8	22.50	14.12	5.04
8 - 10	22.52	13.78	5.18
10 - 12	23.22	13.76	5.11
12 - 14	22.26	13.95	5.40
14 - 16	22.46	13.87	5.35
16 - 18	22.90	13.66	5.34
Leachate	0.14	0.02	0.02
<u>Cooking Lake (Profile 1)</u>			
0 - 1	8.90	7.25	5.77
1 - 2	8.24	5.18	3.92
2 - 3	7.86	3.50	2.22
3 - 4	7.58	3.04	2.17
4 - 5	7.04	2.90	2.17
5 - 6	6.66	2.91	2.30
6 - 8	7.04	2.85	2.16
8 - 10	6.81	2.96	2.24
10 - 12	6.63	3.14	2.20
12 - 14	6.96	2.81	2.22
14 - 16	6.52	3.14	2.10
16 - 18	6.50	3.02	2.24
Leachate	0.02	0.02	0.02

The N^{15} data of Table 32 provide a better indication of the retentive properties of the different horizons. N^{15} analyses were restricted to the top six segments of one selected column for each soil horizon. This was again motivated by a desire to limit the number of spectrometric determinations. The data in Table 32 are presented graphically in Fig. 10 and 11. It is apparent from Table 32 and Fig. 10 that the added N^{15} moved more freely through the Cooking Lake A horizon than the Maleb A. It will be observed (Appendix, item 2) that the Cooking Lake A (Profile 1) was higher in total clay content than the Maleb A (Profile 2). The differences in retentive properties observed here would suggest, therefore, that there was a difference in the clay mineral composition of the two horizons. It is also possible that there is a difference in amount and kind of organic colloids between the two soils. Since the Cooking Lake A displayed a lower tenacity with respect to NH_4^+ retention, it would appear that the differences in N utilization observed in the greenhouse were not primarily due to NH_4^+ retained in difficultly available form by the clay fraction.

The retention pattern in the two B horizons was very similar. In view of the development of the impermeable layer in the Cooking Lake B mentioned earlier, this comparison is only of theoretical interest and the patterns were not depicted.

The retention pattern in the two C horizons (Table 32, Fig. 11) was the reverse of the situation observed in the A horizons. In this case the Cooking Lake C seemed to have a greater affinity for the NH_4^+ ion than did the Maleb C. Appendix, item 2 shows that the total clay content of the two horizons was very similar. Thus the difference in NH_4^+ retention would appear to be attributable to differences in clay mineral type. In view of

TABLE 32. N¹⁵ CONTENT (me./100 g.) OF TOP SIX SOIL
SEGMENTS FOLLOWING LEACHING

Soil Segments (inches)	A Horizon	B Horizon	C Horizon
<u>Maleb (Profile 2)</u>			
0 - 1	2.75	2.56	1.25
1 - 2	0.88	1.35	0.80
2 - 3	0.50	0.54	0.28
3 - 4	0.10	0.08	0.09
4 - 5	0.10	0.06	0.04
5 - 6	0.10	0.06	0.03
<u>Cooking Lake (Profile 1)</u>			
0 - 1	1.40	2.45	1.99
1 - 2	1.09	1.26	1.07
2 - 3	0.78	0.31	0.02
3 - 4	0.40	0.07	0.01
4 - 5	0.25	0.02	0.01
5 - 6	0.19	0.01	0.01

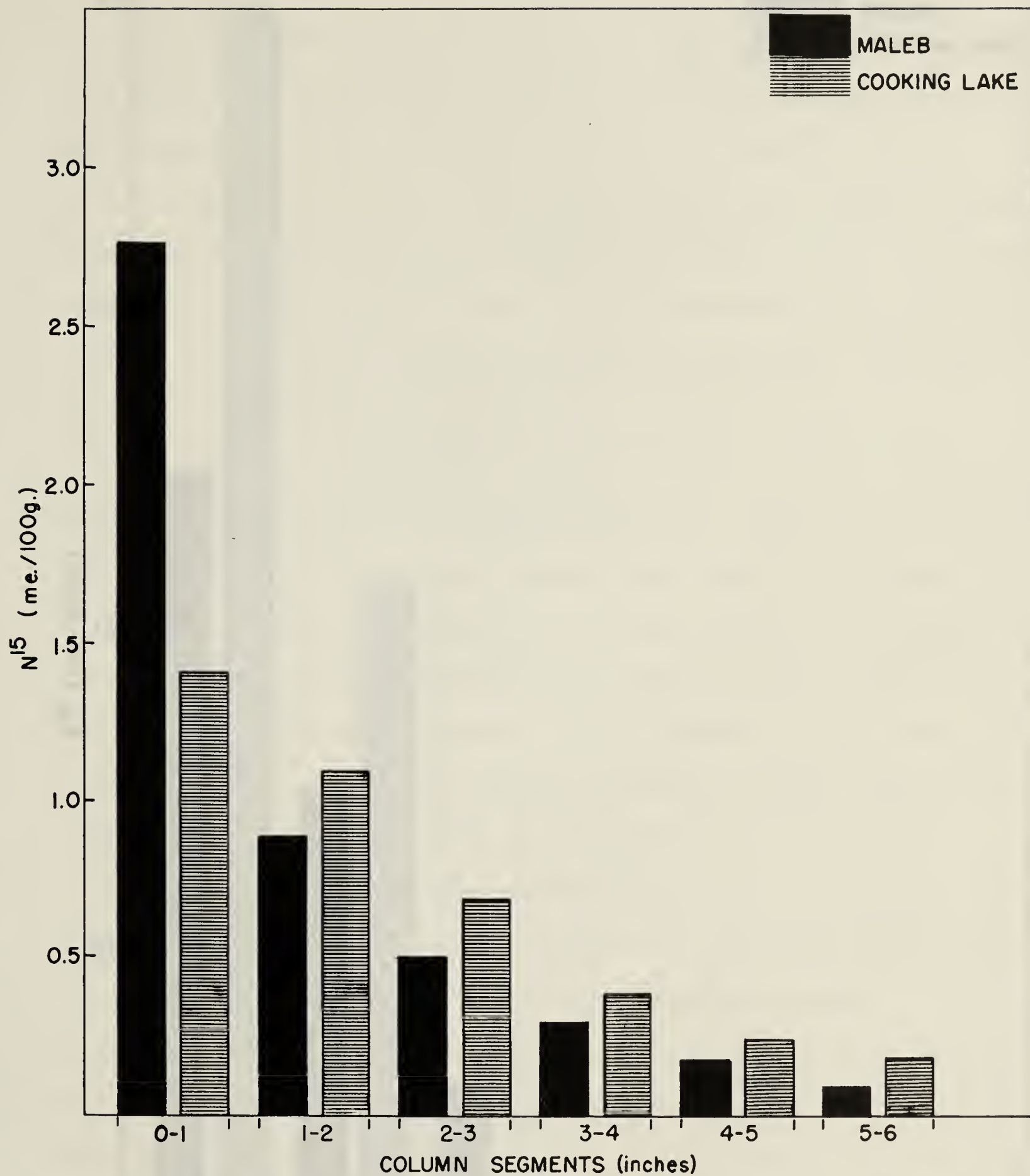


Figure 10. Distribution of added N^{15} in Maleb A (Profile 2) and Cooking Lake A (Profile 1) horizons after leaching with water.

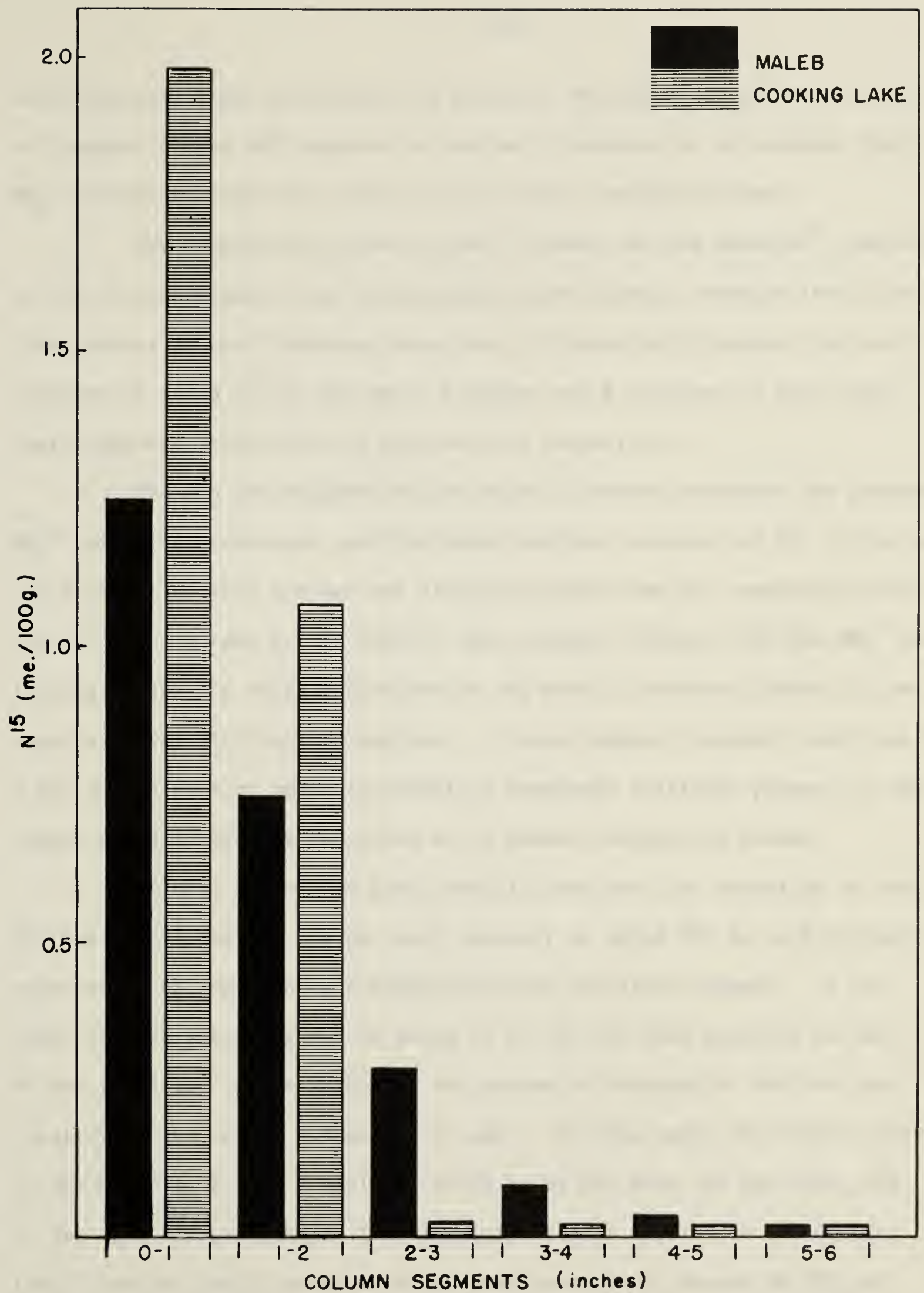


Figure 11. Distribution of added N^{15} in Maleb C (Profile 2) and Cooking Lake C (Profile 1) horizons after leaching.



Figure 1. Distribution of water pH in water of 15 m and 30 m depth. The x-axis represents the water depth (m) and the y-axis represents the frequency. The legend indicates the pH range: pH 6.5-7.5 (light bars) and pH 7.5-8.5 (dark bars).

the relatively small differences in yield of dry matter (Table 15) as well as N uptake (Table 18) observed on the two C horizons it is probable that NH_4^+ retention properties were not the primary deciding factors.

The comparison of the per cent recovery of the added N^{15} (Table 33) in the various segments was interesting to the author. Despite the higher clay content of the C horizons there was a substantially greater per cent recovery of added N^{15} in the two A horizons and B horizons, a fact which again suggests differences in clay mineral composition.

The top two segments of the Maleb A horizon exhibited the greatest NH_4^+ retentive properties, and the total per cent recovery of N^{15} in the top six segments of this horizon was slightly higher than the comparable value for the Cooking Lake A. In view of this stronger affinity for the NH_4^+ ion the high value for total N detected in the Maleb A leachate (Table 31) was surprising and difficult to explain. It would appear, however, that this N was due in part at least to soluble N compounds initially present in the column and dissolved by the water as it passed through the column.

It will be noticed from Table 33 that with the exception of the Cooking Lake A horizon the per cent recovery of added N^{15} in each horizon appeared to be approaching a steady value in the sixth segment. If the value in each sixth segment is taken to be the per cent recovery in each of the remaining twelve inches of the column an estimate of the per cent recovery in the entire column can be made. On this basis the total recovery in the Maleb A, B, and C horizons would be 99 per cent, 83 per cent, and 49 per cent, respectively. This approximation if applied to the Cooking Lake A horizon would result in a per cent recovery in excess of 100 per cent. This is explainable, however, from the fact that the per cent recovery in the sixth segment of this horizon is probably not the steady value. The

TABLE 33. PER CENT RECOVERY OF ADDED N¹⁵ IN THE TOP SIX
SOIL SEGMENTS OF EACH COLUMN
(Average of 2 Replications)

Soil Segments (inches)	A Horizon	B Horizon	C Horizon
<u>Maleb (Profile 2)</u>			
0 - 1	48.40	39.76	21.35
1 - 2	15.49	20.96	13.66
2 - 3	8.80	8.39	4.78
3 - 4	1.76	1.24	1.54
4 - 5	1.76	0.93	0.68
5 - 6	1.76	0.93	0.51
Totals	77.97	72.21	42.52
<u>Cooking Lake (Profile 1)</u>			
0 - 1	25.38	41.96	36.10
1 - 2	19.76	21.58	19.41
2 - 3	14.14	5.31	0.36
3 - 4	7.25	1.20	0.18
4 - 5	4.53	0.34	0.18
5 - 6	3.44	0.17	0.18
Totals	74.50	70.56	56.41

values for the Cooking Lake B and C would be 73 per cent and 59 per cent, respectively. The reason for these estimations is to point out that the per cent recovery in the Maleb and Cooking Lake A horizons was within the limits expected. The values for the two B horizons were also not unreasonable. However, the per cent N^{15} recovery in the two C horizons was remarkably low. The discrepancies were not likely due to volatilization as gaseous NH_3 alone since the soil was kept wet throughout the study. It is possible, however, that some NH_3 was lost by volatilization since the C horizons had an indigenous excess of lime (Table 2) and the parafilm cover was not airtight. Denitrification losses as other volatile N forms are also a possibility since the waterlogged condition of the soil in the columns provided semi-anaerobic conditions. It is unlikely, however, that this was a major factor since even under ideal anaerobic conditions lower soil horizons exhibit less denitrification than do surface horizons (Khan, 1964). The discrepancies could not be attributed to leaching losses since the leachates were essentially unlabelled. It is possible that some of the $N^{15}H_4^+$ was converted to $N^{15}O_3^-$ and was therefore not detected by the Kjeldahl procedure used. The degree of conversion required to account for the discrepancies, however, does not seem feasible, because the columns were allowed to drain for a maximum of 48 hr. following leaching. During the leaching process the soil being saturated should not have allowed appreciable nitrification. Another explanation is that a significant portion of the added NH_4^+ became fixed in these C horizons in a form so highly resistant that even the drastic Kjeldahl digestion was unable to dislodge it. The reason for the low recovery obviously requires further study. Regardless of the mechanism, however, it seems reasonable that this could have been a major factor accounting for the lower N uptake on the Maleb C horizon at

least as compared to the Maleb A (Tables 6 and 18). The yield of N on the Cooking Lake C was also lower than that on the Cooking Lake A at the zero and 150 lb./ac. N rates, but was higher at the 300 lb./ac. N rate.

The data in Table 33 also has important implications for field conditions regarding the application of nitrogenous fertilizers containing the NH_4^+ ion. It will be noted that 48 per cent of the tagged N was retained in the top inch of the Maleb A and 25 per cent in the Cooking Lake A even after being leached by approximately 9 inches of water. Under field conditions the top inch of soil dries quickly, and it is likely that some of the NH_4^+ nitrogen held in this top inch would be subject to volatilization loss as NH_3 . Furthermore, it is unlikely that this NH_4^+ nitrogen would become available to the plant at least during the year of application because of low nitrification and low root activity in the dry surface soil. This also helps to explain why Jansson (1958) in long term pot experiments involving the use of NH_4^+ -N could only detect a 50 per cent recovery of added N in the plant during the initial year of application. The high percentage of NH_4^+ retained in the two A horizons assumes added significance when it is realized that the amount of rainfall on most Alberta soils in the course of a month seldom exceeds 3 inches.

It should be stressed that this study did not determine whether the NH_4^+ retention was due to fixation or adsorption. However, since the Maleb soil retained more NH_4^+ in the column than did the Cooking Lake and yet allowed greater N uptake in the greenhouse, it appears that adsorption was mainly involved. Since the roots were in intimate contact with the total soil mass in the greenhouse experiment, the slow downward movement of NH_4^+ observed in the column study, if due to adsorption, would not be a

major factor. Under field conditions, however, it would probably have an important bearing on nitrogen utilization by a crop. It would appear that immobilization-mineralization phenomena were the dominant factors accounting for the differences observed in the greenhouse experiment.

SUMMARY AND CONCLUSIONS

It is apparent from the foregoing discussion that the Maleb and Cooking Lake soils differed markedly in their reactions with regard to added N. This was reflected in the differences in yield of dry matter (Tables 3 and 15) as well as N uptake (Tables 6 and 18, Fig. 1 and 2). Differences in N utilization also had an indirect effect on the ability of the indicator crop to absorb K and Ca from the two soils (Tables 9, 12, 21, and 24). Despite the use of the high yielding Gateway barley and a relatively high plant stand, the yield of dry matter on the Cooking Lake and Maleb soils was somewhat lower than expected. This suggests that the greenhouse experiment could have been modified to allow for larger pots, more soil, and an even higher plant stand.

Evidence was found that lime generally lowered N uptake on the two soils studied, being more depressive on the Maleb A horizon than on the Cooking Lake A. The response surface for the yield of N on the Cooking Lake A horizon (Fig. 3) showed an initial decrease in yield of N at the two upper N rates as the lime level changed from zero to 5 tons per acre. This observation was difficult to explain. It is likely that a 5 x 5 x 5 composite design would have been preferable to the standard 3 x 3 x 3 design used. This would have facilitated the use of additional levels of each nutrient and would have improved the definition of the response surfaces. The big drawback to this was the fact that this design had never been used at the University of Alberta and there was some doubt as to procedure for statistical analysis. This matter is now receiving attention and the present study confirms that there is need for a design of this type.

There was evidence too that the behaviour of applied lime was similar to that of indigenous free lime in inhibiting N uptake. Lime

depressed dry matter yields significantly on the Maleb A horizon and increased them significantly on the Cooking Lake A. The lime probably corrected a nutrient imbalance on the latter soil. Lime reduced K uptake on the Maleb A horizon but increased it on the Cooking Lake A.

Applied N was the nutrient variable which had the most significant effects, influencing both yield of dry matter and uptake of N, K, and Ca. On the Maleb A horizon, increases in applied N produced increased yields of dry matter at all three levels of lime. On the Cooking Lake A, applied N up to the 150 lb./ac. rate increased dry matter yields but a further increase in N to 300 lb./ac. caused no further increase in dry matter. The effect of applied N on N uptake on the two A horizons closely paralleled the effect on dry matter yields. Increasing N rates produced increasing uptake of K on the Maleb A, but the N effect on K uptake on the Cooking Lake A horizon was erratic. Applied N seemed to produce a weak trend towards increased Ca uptake on the Cooking Lake A, but a strong trend on the Maleb A. Increasing N rates tended in general to produce increased yields of dry matter, N, K, and Ca on the C horizons of both soils.

The effect of K on nutrient uptake was not very marked on these soils. In fact, with the solitary exception of its effect on K uptake on the two A horizons, applied K did not exert a significant influence. In the light of the observations made in the greenhouse studies the first hypothesis was rejected. The converse, that neither native nor applied K had a marked effect on N uptake by plants on the Maleb and Cooking Lake soils, was accepted.

Hypothesis 2 was accepted after the following modification: native lime and added lime will directly or indirectly reduce N uptake on some soils.

Tracer studies on the fate of added N were conducted using $\text{N}^{15}\text{H}_4\text{NO}_3$ as the tracer. Rittenberg's apparatus for converting NH_4^+ to N_2 gas proved unsatisfactory in the present study from the standpoint that the NH_4^+ conversion was tedious and the prepared samples often had considerable air contamination. The apparatus was therefore modified to facilitate the rapid preparation of duplicate samples with very low air contamination. The studies substantiated the hypothesis of Jansson (1958), that added N does not become uniformly diluted with the total soil N. There was evidence of an "active" soil N fraction which corresponded to the nondistillable acid-soluble fraction of Stewart et al. (1963). This is an organic fraction believed to comprise amino acids and acid-soluble humin. The inverse relationship between the inorganic fraction and this nondistillable acid-soluble fraction reported by Stewart et al. (1963) was also substantiated in the present study. The main difference in the fluctuations in these fractions between the two soils was one of extent. Despite a lower total N content in each organic fraction, the Cooking Lake soil immobilized a greater portion of the tagged N in difficultly available form. As a result of these tracer studies the third hypothesis was accepted. That is, fluctuations in the magnitude of the "active" fraction of soil N were reflected in the relative amounts of N taken up from each soil.

Tracer methods involving the use of $\text{N}^{15}\text{H}_4\text{NO}_3$ were also used to study NH_4^+ retention phenomena in the major horizons of the Maleb and Cooking Lake soils. The per cent N^{15} recovery as well as the N^{15} distribution in columns of the two A horizons after leaching showed the retention properties in the two soils to be different, suggesting a difference in the clay mineral composition and possibly a difference in kind and amount of organic colloids. The Maleb A had a greater tenacity for the NH_4^+ ion than

did the Cooking Lake A, but the Cooking Lake C appeared to be superior to the Maleb C in this regard.

It was noteworthy that 48 per cent of the added N^{15} was retained in the top inch of the Maleb A horizon and 25 per cent in the Cooking Lake A even after the passage of 9 inches of water through the soil columns. This could have important implications under field conditions if fertilizers are applied in NH_4^+ form.

Substantial amounts of N^{15} applied to the Maleb and Cooking Lake C horizons could not be accounted for, indicating that large amounts were either fixed, lost by volatilization, or converted to nitrates. For a variety of reasons, it is suggested that the latter two should have been rather small. Further work will be required to confirm the fixation aspect. The low recovery of added N on the C horizons is in accordance with the findings of Viets (1961), who observed low N recovery on high lime soils following the application of N. The comparison of the two B horizons was inconclusive, owing to the development of an impervious layer in the B horizon of the Cooking Lake soil which prevented adequate leaching.

Differences in adsorption properties between the soils probably contributed to the differences in N uptake observed in the greenhouse. The main cause, however, appeared to be attributable to differences in immobilization-mineralization phenomena in the two soils.

BIBLIOGRAPHY

- Allison, F. E., J. H. Doetsch, and E. M. Roller. 1951. Ammonium fixation and availability in Harpster clay loam. *Soil Sci.* 72: 187-200.
- Association of Official Agricultural Chemists. 1955. Official methods of analysis. 8th ed. Washington 4, D.C.
- Axley, J. H., and J. L. Legg. 1960. Ammonium fixation in soils and the influence of potassium on nitrogen availability from nitrate and ammonium sources. *Soil Sci.* 90: 151-156.
- Barshad, I. 1954. Cation exchange in micaceous minerals. II. Replaceability of NH_4^+ and K^+ from vermiculite, biotite, and montmorillonite. *Soil Sci.* 78: 57-76.
- Bear, F. E. 1950. Cation-anion relationships in plants and their bearing on crop quality. *Agron. Jour.* 42: 176-178.
- Bouyoucos, G. J. 1951. A recalibration of the hydrometer method for making mechanical analysis of soils. *Agron. Jour.* 43: 434-438.
- Bower, C. A. 1950. Fixation of ammonium in difficultly exchangeable form under moist conditions by some soils of semi-arid regions. *Soil Sci.* 70: 375-383.
- Bremner, J. M. 1949. Studies on soil organic matter: 1. The chemical nature of soil organic nitrogen. *J. Agr. Sci.* 39: 183-193.
- Bremner, J. M. 1950. The amino acid composition of the protein material in soil. *Biochem. Jour.* 47: 538-542.
- Bremner, J. M., and K. Shaw. 1954. Studies on the estimation and decomposition of amino sugars in soil. *J. Agr. Sci.* 44: 152-159.
- Bremner, J. M. 1959. Determination of fixed ammonium in soil. *J. Agr. Sci.* 52: 147-160.
- Brown, W. G., E. O. Heady, J. T. Pesek, and J. A. Stritzel. 1956. Production functions, isoquants, isoclines, and economic optima in corn fertilization for experiments with two and three variable nutrients. Ag. Exp. Station, Iowa State College. Research Bulletin 441.
- Capindale, J. B., and D. H. Tomlin. 1957. Use of argon peak for air correction in mass spectrometric measurement of nitrogen. *Nature* 180: 701.
- Chao Tsun Tien, M. E. Harward, and S. C. Fang. 1960. Movement of S^{35} tagged sulphate through soil columns. Ph. D. Thesis, Oregon State College.

- Cheng, H. H., and L. T. Kurtz. 1963. Chemical distribution of added nitrogen in soils. *Soil Sci. Soc. Amer. Proc.* 27: 312-316.
- Cheng, K. L., and R. H. Bray. 1951. Determination of calcium and magnesium in soil and plant material. *Soil Sci.* 72: 449-458.
- Crable, G. F., and N. F. Kerr. 1957. Reaction of oxygen in a mass spectrometer to form carbon monoxide. *Analyt. Chem.* 29: 1281.
- Dashevskiy, L. I. 1961. Method of extracting adsorbed ammonium from soils. *Soviet Soil Sci.* 11: 1260-1262.
- Davidson, D. I., F. J. Sowden, and H. J. Atkinson. 1951. Application of paper chromatography to identification and quantitative estimation of amino acids in soil organic matter fractions. *Soil Sci.* 71: 347-352.
- Dhariwal, A. P. S., and F. J. Stevenson. 1958. Determination of fixed ammonium in soils. *Soil Sci.* 86: 343-349.
- Drake, M., and J. M. White. 1961. Influence of nitrogen on the uptake of calcium. *Soil Sci.* 91: 66-69.
- Engelhardt, Eva. 1959. Determination of calcium by versene titration. *Laboratory Procedures, Agricultural Soil and Feed Testing Laboratory, Univ. of Alberta*: p. 9.
- Goettel, A. 1961. The potassium status of some Alberta soils. Unpublished M. Sc. Thesis, Univ. of Alberta, Edmonton.
- Hader, J., M. E. Harward, D. D. Mason, and D. P. Moore. 1957. An investigation of some of the relationships between Cu, Fe, and Mo in the growth and nutrition of lettuce. 1. Experimental design and statistical methods for characterizing response surfaces. *Soil Sci. Soc. Amer. Proc.* 21: 59-64.
- Hausmann, W. 1899. Über die vertheilung des stickstoffs im eiweissmolekül. *Z. Physiol. Chem., Hoppe-Seyler's*, 27: 95-108.
- Hewitt, E. J. 1952. Sand and water culture methods used in the study of plant nutrition. *Common. w. Agr. Bur. Tech. Comm.* 22: p. 86.
- Hinman, W. C. 1963. Fixed ammonium in some Saskatchewan soils. *Can. J. Soil Sci.* 44: 151-157.
- Hoering, T. C. 1955. Variations of nitrogen-15 abundance in naturally occurring substances. *Science* 122: 1233.
- Hüser, R., K. Habfast, and M. V. Bradke. 1960. Die bestimmung der stickstoffisotopenhäufigkeit im ammoniastickstoff. *Z. Anal. Chem.* 176: No. 6. pp. 429-436.

- Jansson, Sven L. 1958. Tracer studies on nitrogen transformation in soil with special attention to mineralization immobilization relationships. Ann. Roy. Agr. Coll. Sweden. 24: 101-361.
- Joshi, N. V., and S. G. Joshi. 1953. Soil fertility and microbial activity. J. Indian Soc. Soil Sci. 1. 15-20.
- Kamen, M. D. 1957. Isotopic tracers in biology. 3rd Ed., Academic Press. New York and London. pp. 345-348.
- Kojima, R. J. 1947. Soil organic nitrogen. 1. Nature of the organic nitrogen in a muck soil from Geneva, New York. Soil Sci. 64: 157-165.
- Legett, G. E., and C. D. Moore. 1962. The aeration-recovery method for determining NH_4^+ fixation by soils under moist conditions. Soil Sci. Soc. Amer. Proc. 26: 160.
- Lyon, T. L., H. O. Buckman, and N. C. Brady. 1955. The nature and properties of soils. 5th Ed., Macmillan Co., New York. Chap. 16.
- Martin, A. E., E. F. Henzell, et al. 1963. Isotopic studies on the uptake of nitrogen by pasture grasses. 1. Recovery of fertilizer nitrogen from the soil: plant system using Rhodes grass in pots. Australian J. Soil Res. Vol. 1, No. 2: 169-184.
- Mason, J. L. 1962. Report on potassium fertilization. Soil Horizons 3: No. 3, p. 20.
- McBeth, I. G. 1917. Fixation of ammonia in soils. J. Ag. Res. 9: 141-155.
- McLeod, L. B., and R. B. Carson. 1964. Effect of potassium on the utilization of NO_3^- and NH_4^+ nitrogen by alfalfa and orchardgrass grown in a nutrient solution culture. Unpublished data. Can. Dept. of Agriculture, Nappan, Nova Scotia.
- Moore, D. T., M. E. Harward, D. D. Mason, J. Hader, W. L. Lott, and W. A. Jackson. 1957. Response surface of growth and accumulations of Cu and Fe. Soil Sci. Soc. Amer. Proc. 21: 65-74.
- Mortland, M. M. 1958. Reactions of ammonia in soils. Advances in agronomy. Vol. 10: p. 325.
- Neilson, K. F., R. B. Carson, and I. Hoffman. 1963. A study of ion interactions in the uptake of nitrogen, phosphorus, potassium, calcium, chlorine, and sulphur by corn. Soil Sci. 95: 315-321.
- Nommik, H. 1957. Fixation and defixation of ammonium in soils. Acta Agr. Scand. 7: 395-436.
- Owens, L. D. 1960. Nitrogen movement and transformations in soils as evaluated by a lysimeter study utilizing isotopic nitrogen. Soil Sci. Soc. Amer. Proc. 24: 372-376.

- Pawluk, S. 1955. The exchangeable cation status of some west central Alberta soils. M. Sc. Thesis, Univ. of Alberta, Edmonton.
- Purvis, E. R., and Micah W. M. Leo. 1961. Rapid procedure for estimating potentially available soil nitrogen under greenhouse conditions. *Ag. and Food Chemistry* 9: 15.
- Putnam, Hugh D., and E. E. Schmidt. 1959. Studies of the free amino acid fraction of soils. *Soil Sci.* 87: 22-27.
- Rankama, K. 1954. Isotope geology. McGraw Hill Book Co., New York. pp. 234-238.
- Reitemeier, R. F. 1951. Soil potassium. *Adv. in Agron.* 3: 113-164.
- Rendig, V. V. 1951. Fractionation of soil organic nitrogen and factors affecting distribution. *Soil Sci.* 71: 253-267.
- Rittenberg, D. 1948. Preparation and measurement of isotopic tracers. (Edwards, Ann Harbour, Michigan.) pp. 31-39.
- Robinson, P., and K. F. Nielson. 1960. Composite designs in agricultural research. *Can. J. Soil Sci.* 40: 168-176.
- Rodrigues, G. 1954. Fixed ammonia in tropical soils. *J. Soil Sci.* 5: 264-274.
- Russell, E. W. 1961. Soil conditions and plant growth. 9th Ed. Longmans. Chap. 3.
- Russell, J. S., C. W. Bourg, and H. F. Rhoades. 1954. Effect of nitrogen fertilizer on the N, P, and cation contents of brome grass. *Soil Sci.* 18: 292.
- Shear, C. B., H. L. Crane, and A. T. Myers. 1946. Nutrient element balance: A fundamental concept in plant nutrition. *Proc. Am. Soc. Hort. Sci.* 47: 239-248.
- Sims, A. D., and E. C. Cocking. 1958. Assay of isotopic nitrogen by mass spectrometer. *Nature* 181: 474.
- Snedecor, G. W. 1959. Statistical methods. Iowa State College Press.
- Soloway, S. 1951. Reference standard for mass spectrometric analysis of nitrogen. *Analyt. Chem.* 23: 386.
- Sprinson, D. D., and D. Rittenberg. 1948. Preparation of gas samples for mass spectrometric analyses of isotope abundance. A symposium on preparation and measurement of isotopes for use in biochemistry. U.S. Naval Med., Bull. Suppl. pp. 82-83.
- Stanford, G., and J. D. Dement. A method for measuring short-term nutrient absorption by plants. *Soil Sci. Soc. Amer. Proc.* 21: 612-617.

- Stanford, G., and W. H. Pierre. 1946. The relationship of potassium fixation to ammonium fixation. *Soil Sci. Soc. Amer. Proc.* 11: 155-160.
- Stephen, R. C., and J. S. Waid. 1963. Pot experiments on urea as a fertilizer. 1. A comparison of responses by various plants. *Plant and Soil*. 18: 309-316.
- Stevenson, F. J. 1956. Isolation and identification of some amino compounds in soils. *Soil Sci. Soc. Amer. Proc.* 20: 201-204.
- Stevenson, F. J. 1957. Distribution of the forms of nitrogen in some soil profiles. *Soil Sci. Soc. Amer. Proc.* 21: 283-287.
- Stevenson, F. J., and A. P. S. Dhariwal. 1959. Distribution of fixed ammonium in soils. *Soil Sci. Soc. Amer. Proc.* 23: 121-125.
- Stewart, B. A., L. K. Porter, and D. D. Johnson. 1963. Immobilization and mineralization of nitrogen in several organic fractions of soil. *Soil Sci. Soc. Amer. Proc.* 27: 302-304.
- Synghal, K. N., J. A. Toogood, and C. F. Bentley. 1959. Assessing nitrogen requirements of some Alberta soils. *Can. J. Soil Sci.* 39: 120-128.
- Taras, Michael, K. 1958. In Boltz, David F. ed. *Colorimetric determination of nonmetals*. New York, N. Y. Interscience Publisher, Inc. pp. 77-160.
- Urey, Harold C. 1947. The thermodynamic properties of isotopic substances. 1. *Chem. Soc.* 562-581.
- Van Slyke, D. D. 1911. The analysis of proteins by determination of the chemical groups characteristic of the different amino acids. *J. Biol. Chem.* 10. 15-55.
- Viets, F. G., Jr. 1960. Recovery of fertilizer nitrogen on irrigated and dryland soils of the Western United States. *Trans. Intern. Congr. Soil Sci.* 7th Congr. Madison 2: 486-493.
- Walker, W. M., and John Pesek. 1963. Chemical composition of Kentucky Bluegrass (*Poa pratensis*) as a function of applied nitrogen, phosphorus, and potassium. *Agron. Jour.* 55: 247-250.
- Weeks, W. D. et al. 1959. The effect of varying rates of N and K on the mineral composition of McIntosh foliage and fruit color. *Soils and Fertilizers* 22, Ab. 1447.
- Welch, L. F., and A. D. Scott. 1960. Nitrification of fixed ammonium in clay minerals as affected by added potassium. *Soil Sci.* 90: 79-85.
- White, W. C., and J. Pesek. 1959. Nature of residual N in Iowa soils. *Soil Sci. Soc. Amer. Proc.* 23: 39-42.

- Willard, H. H., L. L. Merritt, Jr., and J. A. Dean. 1960. Instrumental methods of analysis. D. Van Nostrand Company, Inc. pp. 283-301.
- Woodruff, C. M. 1955. The energies of replacement of calcium by potassium in soils. Soil Sci. Soc. Amer. Proc. 19: 167-171.
- Wyatt, F. A., J. D. Newton, W. E. Bowser, and W. Odymsky. 1944. Soil survey of Wainwright and Vermilion sheets. p. 29.
- Young, J. L., and R. A. Cattoni. 1962. Mineral fixation of anhydrous NH_3 by air-dry soils. Soil Sci. Soc. Amer. Proc. 26: 147.
- Young, J. L. 1962. Inorganic soil nitrogen and carbon:nitrogen relations of some Pacific Northwest soils. Soil Sci. 93: 397-404.

APPENDIX 1

MODIFIED HEWITT'S NUTRIENT SOLUTION (Hewitt, 1952)*

KH_2PO_4	2.00 g.
NaCl	0.40 g.
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	2.00 g.
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	2.00 g.
Sequestrene	0.12 g.
H_3BO_3	2.00 mg.
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	6.20 mg.
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	3.50 mg.
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	2.10 mg.
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.05 mg.
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.10 mg.
Distilled H_2O	20 litres

* Modifications made were as follows:

1. Omission of KNO_3
2. Substitution of Sequestrene for Ferric citrate

APPENDIX 2

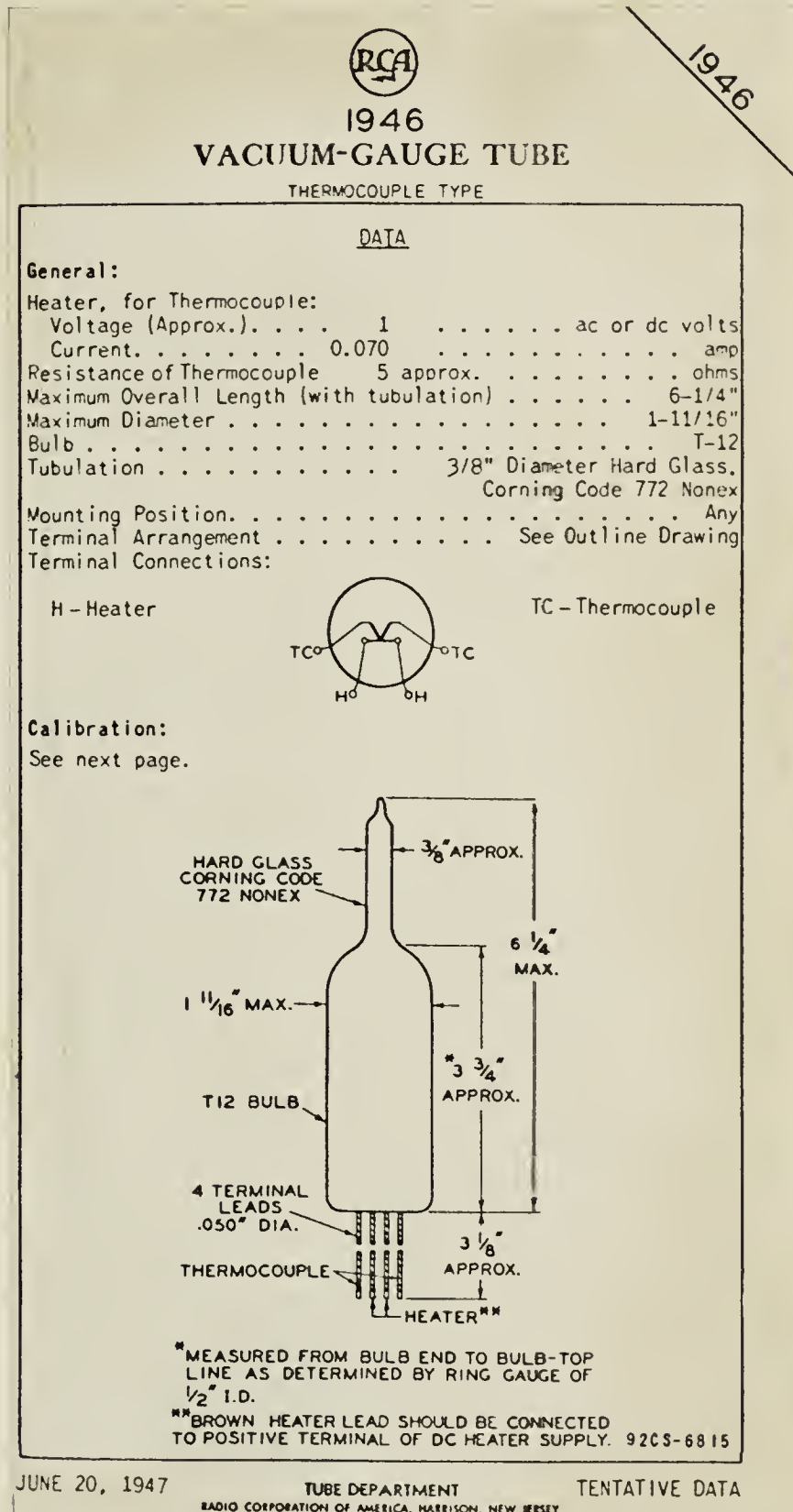
MECHANICAL ANALYSIS OF SOILS UNDER STUDY *

Samples	% Sand	% Silt	% Clay
Maleb 1A	49	26	25
Maleb 1B	50	25	26
Maleb 1C	47	23	30
Maleb 2A	62	23	16
Maleb 2B	42	28	30
Maleb 2C	49	19	32
Maleb 3A	52	23	25
Maleb 3B	52	19	30
Maleb 3C	41	24	35
Elnora 1A	68	19	13
Elnora 1B	60	14	26
Elnora 1C	31	40	29
Elnora 2A	51	26	23
Elnora 2B	34	30	26
Elnora 2C	42	18	40
Elnora 3A	58	28	14
Elnora 3B	49	16	35
Elnora 3C	46	17	38
Cooking Lake 1A	50	30	20
Cooking Lake 1B	49	17	34
Cooking Lake 1C	44	23	32
Cooking Lake 2A	52	28	30
Cooking Lake 2B	42	24	34
Cooking Lake 2C	34	28	38
Cooking Lake 3A	44	31	25
Cooking Lake 3B	44	16	40
Cooking Lake 3C	47	19	35

* Bouyoucos, 1951.

APPENDIX 3

TUBE CHARACTERISTICS OF THERMOCOUPLE VACUUM GAUGE



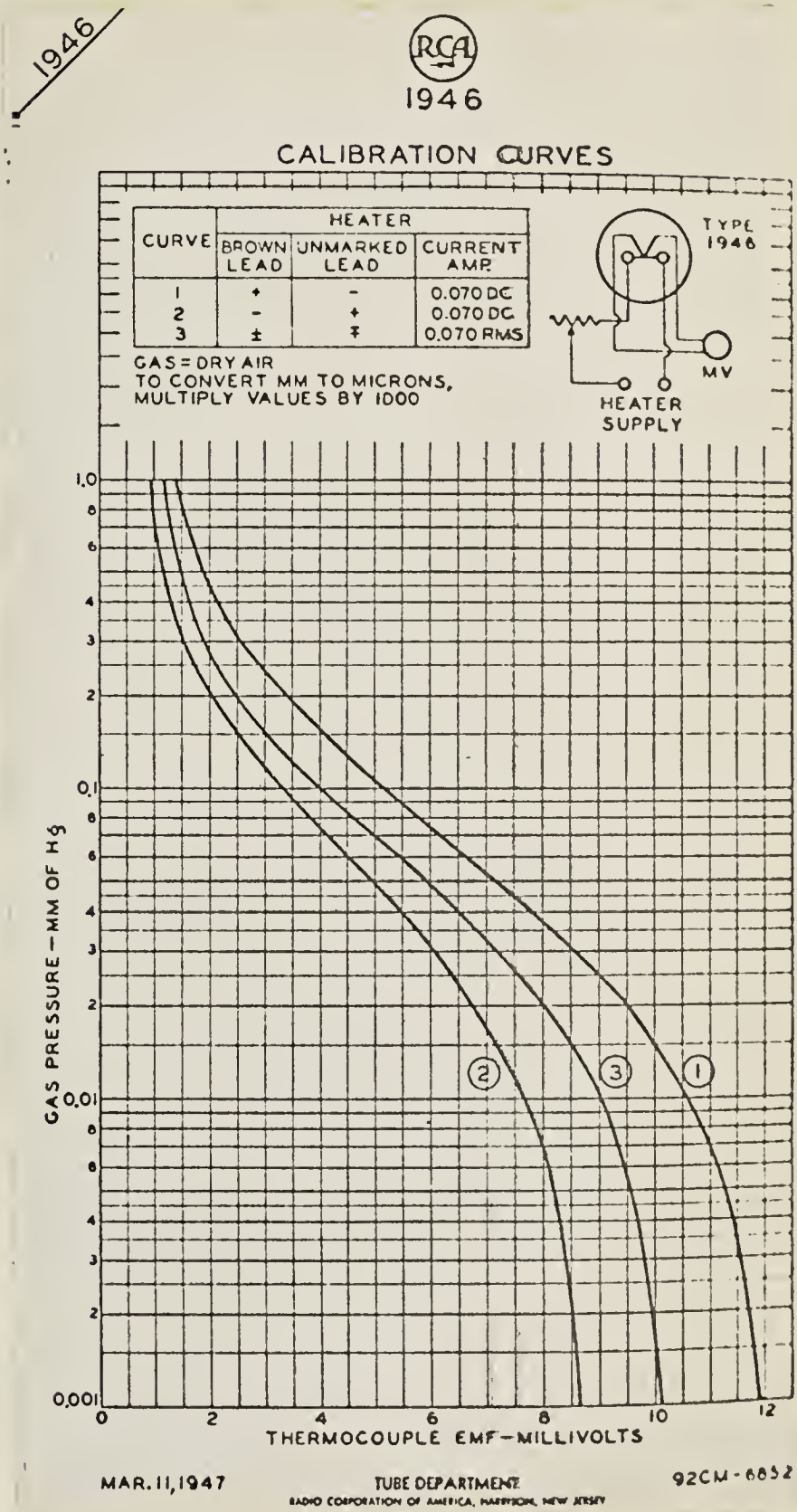
JUNE 20, 1947

TUBE DEPARTMENT
RADIO CORPORATION OF AMERICA, HARRISON, NEW JERSEY

TENTATIVE DATA

APPENDIX 4

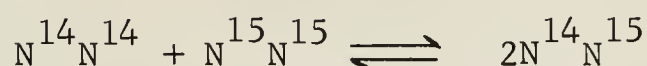
CALIBRATION CURVES FOR THERMOCOUPLE VACUUM GAUGE



APPENDIX 5

DERIVATION OF EQUATION FOR COMPUTING ATOM % N¹⁵ IN A SAMPLE CONTAINING BOTH NITROGEN ISOTOPES

N¹⁵ and N¹⁴ exist in dynamic equilibrium in accordance with the equation:



The equilibrium constant K for this reaction is given by

$$\frac{[N^{14}N^{15}]^2}{[N^{14}N^{14}][N^{15}N^{15}]} = 4 \quad (\text{Rittenberg, 1946})$$

$$\text{Now if } \frac{[N^{14}N^{15}]}{[N^{14}N^{14}]} \frac{[N^{14}N^{15}]}{[N^{15}N^{15}]} = 4$$

$$\text{Then } \frac{[N^{14}N^{15}]}{[N^{14}N^{14}]} = \frac{4[N^{15}N^{15}]}{[N^{14}N^{15}]}$$

$$\text{Let } \frac{[N^{14}N^{14}]}{[N^{15}N^{14}]} = R$$

$$\text{Then } \frac{[N^{15}N^{15}]}{[N^{14}N^{15}]} = \frac{1}{4R} \quad \text{Eq. 1}$$

$$\begin{aligned} \text{Atom \% N}^{15} &= \frac{\text{No. of atoms N}^{15}}{\text{Total No. of N atoms}} \times 100 \\ &= \frac{([N^{14}N^{15}] + 2[N^{15}N^{15}]) \times 100}{2([N^{14}N^{14}] + [N^{14}N^{15}] + [N^{15}N^{15}])} \end{aligned} \quad \text{Eq. 2}$$

Now dividing the numerator and denominator by [N¹⁴N¹⁵] and substituting

$$R = \frac{[N^{14}N^{14}]}{[N^{15}N^{14}]}$$

equation 2 reduces to:

$$\frac{\left(1 + \frac{1}{2R} \times 100\right)}{2 \left[R + 1 + \frac{1}{4R}\right]} \quad \text{Eq. 3}$$

$$\text{Atom \% N}^{15} = \frac{\left[\frac{2R}{4R^2} + \frac{1}{4R} + 1\right] \times 100}{2R}$$

APPENDIX 5 (Continued)

$$= \frac{[2R + 1] \times 100}{[4R^2 + 4R + 1]}$$

$$= \frac{[2R + 1] \times 100}{[2R + 1] [2R + 1]}$$

$$\text{Therefore Atom \% N}^{15} = \frac{100}{[2R + 1]}$$

Where R is the ratio of the 28 peak intensity to 29 peak intensity as monitored on the mass spectrometer.

APPENDIX 6

CALCULATION OF ATOM PER CENT N¹⁵ FROM MASS SPECTROMETER DATA

<u>Residuals</u>		
<u>28 Peak Intensity</u>	<u>29 Peak Intensity</u>	<u>32 Peak Intensity</u>
477	27	39

<u>Run</u>		
<u>28 Peak Intensity</u>	<u>29 Peak Intensity</u>	<u>32 Peak Intensity</u>
78100	14610	60
73500	13650	
71300	13260	
69200	12930	
67200	12570	
65200	12210	
63700	11880	
61700	11490	
59600	11160	
58100	10830	

Net Values (Run-Residuals)

<u>28 Peak Intensity</u>	<u>29 Peak Intensity</u>	<u>32 Peak Intensity</u>
77623	14583	21
73023	13623	
70823	13233	
68723	12903	
66723	12543	
64723	12183	
63223	11853	
61223	11463	
59123	11133	
57623	10803	

APPENDIX 6 (Continued)

<u>R (Ratio 28/29)</u>	<u>Δ (Deviation from Mean)</u>	<u>$\Delta^2 \times 10^{-6}$</u>
5.323	0.008	64
5.360	0.029	841
5.352	0.021	441
5.326	0.005	25
5.320	0.011	121
5.312	0.019	361
5.334	0.003	9
5.341	0.010	100
5.311	0.020	400
5.334	0.003	9

Mean R = 5.331

$$\text{Std. Deviation} = \sqrt{\frac{\sum \Delta^2}{N - 1}} = \sqrt{\frac{2371 \times 10^{-6}}{9}} = 16.22 \times 10^{-3}$$

$$\% \text{ Std. Deviation} = \frac{16.22 \times 10^{-3}}{5.331} \times 100 = 0.30$$

$$\text{Atom \% N}^{15} = \frac{100}{(2R + 1)} = \frac{100}{11.622} = 8.574$$

$$\% \text{ Air Contamination} = \frac{21 \times 6.3^* \times 100}{77623} = 0.17$$

$$\text{Corrected Value} = (8.574 - 0.38^{**}) \times 1.0017 = 8.194 \text{ Atom \% N}^{15}$$

* Correction factor accounting for mass discrimination of O_2 with respect to N_2 by the mass spectrometer (Appendix 7).

** Normal abundance of N^{15} as per Rankama (1954).

APPENDIX 7

CALIBRATION OF THE MASS SPECTROMETER FOR INHERENT DISCRIMINATION OF MASS 28
WITH RESPECT TO MASS 32

Air correction of the nitrogen gas samples analyzed was done by monitoring the mass 32 peak due to oxygen and then computing the resultant N contribution to the peaks at masses 28 and 29. Although there is approximately four times as much nitrogen in air as oxygen, it is incorrect to assume that the air contribution to the mass 28 peak is four times the peak intensity of the oxygen peak. This is an invalid assumption since the probability of ionization of oxygen and nitrogen is not the same. It is found in actual practice that each mass spectrometer discriminates inherently against the mass 32 ions with respect to the ions at mass 28. The actual ratio of mass 28 to mass 32 must therefore be determined for each spectrometer by analysis of a sample of air. The following data illustrate how this was done for the 6 inch radius 60⁰ Magnetic Analyzer.

<u>Residuals</u>	
<u>28 Peak Intensity</u>	<u>32 Peak Intensity</u>
455	19.5

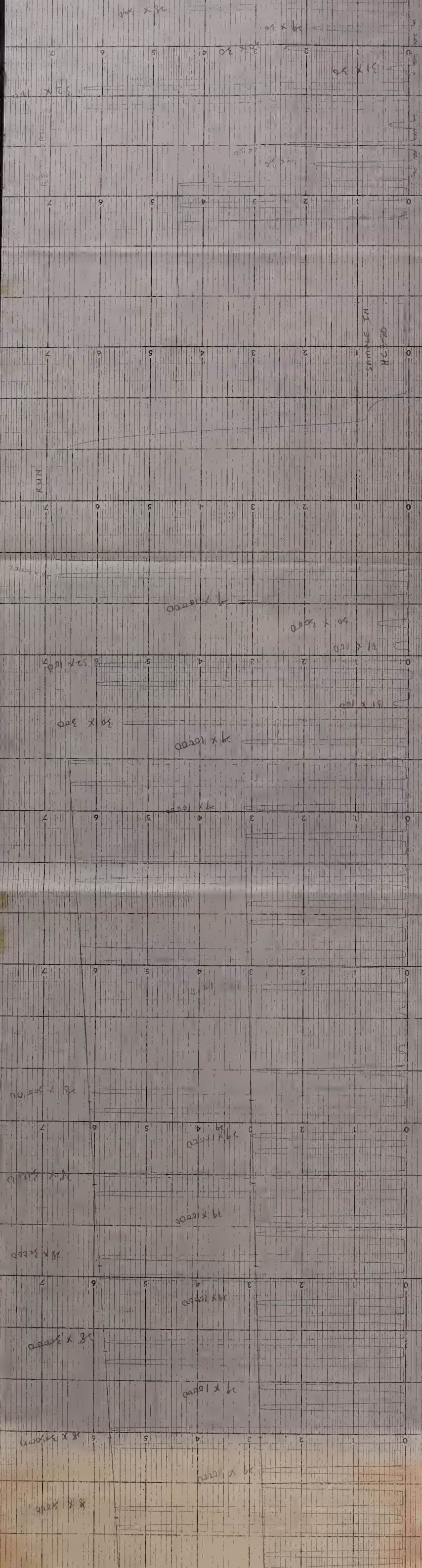
<u>Run</u>	
<u>28 Peak Intensity</u>	<u>32 Peak Intensity</u>
71700	11100
67500	10590
63200	9990
59000	9300
55000	8760

APPENDIX 7 (Continued)

Net Values (Residuals Subtracted)

<u>28 Peak Intensity</u>	<u>32 Peak Intensity</u>	<u>Ratio 28/32</u>
71245	11080.5	6.43
67045	10570.5	6.34
62745	9980.5	6.29
58545	9280.5	6.31
54545	8740.5	6.24

Therefore average air correction factor = 6.32. Similar calibration procedures conducted on the 12 inch 90° Magnetic Analyzer revealed that the correction factor for this instrument was 6.10.



B29833